



PHD

Modelling nitrification in the River Zarka of Jordan

Abumoghli, Iyad

Award date:
1993

Awarding institution:
University of Bath

[Link to publication](#)

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

Copyright of this thesis rests with the author. Access is subject to the above licence, if given. If no licence is specified above, original content in this thesis is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International (CC BY-NC-ND 4.0) Licence (<https://creativecommons.org/licenses/by-nc-nd/4.0/>). Any third-party copyright material present remains the property of its respective owner(s) and is licensed under its existing terms.

Take down policy

If you consider content within Bath's Research Portal to be in breach of UK law, please contact: openaccess@bath.ac.uk with the details. Your claim will be investigated and, where appropriate, the item will be removed from public view as soon as possible.

**MODELLING NITRIFICATION
IN THE
RIVER ZARKA OF JORDAN**

**SUBMITTED BY
IYAD ABUMOGHLI**

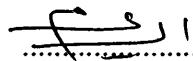
**FOR THE DEGREE OF PhD
OF THE UNIVERSITY OF BATH**

1993

COPYRIGHT

"Attention is drawn to the fact that copyright of this thesis rests with its author. This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with its author and that no quotation from the thesis and no information derived from it may be published without the prior written consent of the author"

"This thesis may be made available for consultation within the University Library and may be photocopied or lent to other libraries for the purposes of consultation".

A handwritten signature in black ink, consisting of stylized cursive letters, positioned above a horizontal dotted line.

UMI Number: U601528

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U601528

Published by ProQuest LLC 2013. Copyright in the Dissertation held by the Author.
Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against
unauthorized copying under Title 17, United States Code.



ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

UNIVERSITY OF LATH LIBRARY		
34	21 MAR 1994	
PHD		

5078461

TO MY PARENTS

TO MY WIFE

TO BAYAN AND DIANA

TO MY BROTHERS AND SISTERS

TO ASHLEY

TABLE OF CONTENTS:

ACKNOWLEDGEMENTS	xi
SUMMARY	xii

CHAPTER ONE: INTRODUCTION

1.1- INTRODUCTION	1
1.2- THE RIVER ZARKA SYSTEM	3
1.3- IMPORTANCE OF NITRIFICATION	7
1.4- MATHEMATICAL MODELLING	9
1.5- STUDY OBJECTIVES	10
1.6- CONCLUSIONS	11

CHAPTER TWO: LITERATURE REVIEW

2.1- INTRODUCTION	18
2.2- NITRIFICATION	21
2.3- DENITRIFICATION	24
2.4- MODELLING	27
2.4.1- QUAL 2EU MODEL	31
2.4.2- BLACKWATER MODEL	35
2.4.3- COMPARISON OF THE BLACKWATER AND QUAL 2EU MODELS	40
2.5- FACTORS AFFECTING NITRIFICATION	41
2.5.1- BACTERIA	42
2.5.2- TEMPERATURE	45
2.5.3- DISSOLVED OXYGEN (DO)	48
2.5.4- pH VALUE	52
2.5.5- ALGAE AND LIGHT	54
2.5.6- BIOCHEMICAL OXYGEN DEMAND, (BOD)	56
2.5.7- CHEMICAL OXYGEN DEMAND (COD)	58
2.5.8- RIVER BED SEDIMENT	58
2.5.9- PROCESS INHIBITION	59
2.5.10- GENERAL	65

CHAPTER THREE: MATERIALS AND METHODS

3.1- SITES DESCRIPTION AND METHODOLOGY	67
3.1.1- SITES DESCRIPTION	67
3.1.2.1- Sample collection	70
3.1.2.2- Physical and chemical parameters	71
3.1.2.2.1- Temperature and Dissolved Oxygen ...	71
3.1.2.2.2- pH-Value	72
3.1.2.2.3- Biochemical Oxygen Demand, BOD ₅ .	72
3.1.2.2.4- Nitrate, NO ₃ ⁻	72
3.1.2.2.5- Nitrite, NO ₂ ⁻	73

TABLE OF CONTENTS (continue):

3.1.2.2.6- Ammonium ion Determination	74
3.1.2.2.7- Total Organic Carbon, TOC (PV)	74
3.1.2.2.8- Chemical Oxygen Demand, COD	74
3.1.2.2.9- Turbidity	75
3.1.2.2.10- Salinity as Chloride	75
3.1.2.2.11- Hydrogen Sulphide, H ₂ S	75
3.1.2.3- BIOLOGICAL DETERMINATIONS	76
3.1.2.3.1- Bacterial Count	76
3.1.2.3.1.1- Nitrifying Bacteria	76
3.1.2.3.1.1. a- Ammonia Oxidizers	76
3.1.2.3.1.1.b- Nitrite Oxidizers	77
3.1.2.3.1.2- Denitrifying Bacteria	77
3.1.2.3.2- Chlorophyll "a"	77
3.1.2.4- Sediment content analysis	78
3.1.2.4.1- Nitrogenous compounds	78
3.1.2.4.2- Bacterial content	78
3.2- BATCH EXPERIMENTS	78
3.2.1- River Zarka water and activated sludge effluent	79
3.2.2- Pure culture experiment	82
3.2.2.1- Media of denitrifying bacteria	84
3.2.2.2- Media of nitrifying bacteria	85

CHAPTER FOUR: WATER QUALITY OF RIVER ZARKA

4.1- INTRODUCTION	87
4.2- RIVER WATER (SITE 2 TO SITE 9)	91
4.2.1- pH- VALUE	91
4.2.3- TEMPERATURE	91
4.2.3- DISSOLVED OXYGEN	92
4.2.4- NITRATE NO ₃ ⁻ , NITRITE NO ₂ ⁻ , AND AMMONIA NH ₄ ⁺	94
4.2.5. PHOSPHATE, PO ₄ ⁻³	95
4.2.6- SALINITY AS CHLORIDE, Cl ⁻	96
4.2.7- TOTAL ORGANIC CARBON (TOC) CHEMICAL OXYGEN DEMAND (COD), AND BIOCHEMICAL OXYGEN DEMAND (BOD ₅)	96
4.2.8- TURBIDITY	100
4.2.9- HYDROGEN SULPHIDE (HS ⁻)	102
4.2.10- CHLOROPHYLL "a"	102
4.2.11- BACTERIAL COUNT	103
4.3- AL-SUKHNEH STREAM (THE TRIBUTARY) (SITE 10)	105

**CHAPTER FIVE: ON-SITE AND LABORATORY BATCH
EXPERIMENTS**

5-1 INTRODUCTION	107
5.2- PURE CULTURE EXPERIMENTS	108
5.3- ACTIVATED SLUDGE (AS) WASTEWATER EFFLUENT	114

TABLE OF CONTENTS (continue):

5.4- RIVER ZARKA WATER	127
5.4.1- EFFECT OF TEMPERATURE	127
5.4.2- EFFECT OF CELL CONCENTRATION	131
5.4.3- EFFECT OF LIGHT	144
5.4.4- DIURNAL TEMPERATURE AND OXYGEN VARIATION	148
5.4.5- EFFECT OF RIVER BED SEDIMENT	151
5.4.6- EFFECT OF AERATION AND OXYGEN CONCENTRATION	157
5.4.7- TOTAL SUSPENDED SOLIDS	160
5.5- SUMMARY AND CONCLUSIONS	161

CHAPTER SIX: APPLICATION OF TWO RIVER WATER QUALITY MODELS TO THE ZARKA RIVER

6.1- INTRODUCTION	167
6.2- DESCRIPTION	168
6.3- APPLICATION OF THE TWO MODELS TO THE RIVER ZARKA	169
6.4- CONCLUSIONS	180

CHAPTER SEVEN: THE ZARKA MODEL

7.1- INTRODUCTION	182
7.2- MODEL ASSUMPTIONS	186
7.3- THE ZARKA MODEL	187
7.3.1- BIOCHEMICAL OXYGEN DEMAND (BOD)	188
7.3.2- AMMONIUM NH_4^+	189
7.3.3- NITRATE NO_3^-	192
7.3.4- DISSOLVED OXYGEN (DO)	195
7.3.5- TEMPERATURE DEPENDENCE	202
7.4- EVALUATING THE PREDICTIVE PERFORMANCE OF THE ZARKA MODEL	205
7.5- CONCLUSIONS	211

CHAPTER EIGHT: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1- INTRODUCTION:	214
8.2- LITERATURE DISPUTES:	215
8.3- FACTORS AFFECTING NITRIFICATION IN THE RIVER ZARKA:	216
8.4- APPLICATION OF OTHER WATER QUALITY MODELS:	219
8.5- THE ZARKA MODEL:	220
8.6- RECOMMENDATIONS FOR FUTURE WORK:	221

APPENDIX:	224
------------------------	-----

BIBLIOGRAPHY	240
---------------------------	-----

LIST OF FIGURES:

FIGURE 1.1: Surface water basins in Jordan.	2
FIGURE 1.2: Flow rates of the Zarka river and the tributary (Al-Sukhneh stream).	3
FIGURE 1.3: Nitrate and ammonium concentrations in the Zarka and its tributary.	5
FIGURE 1.4: River Zarka in Jordan	7
PHOTOS OF THE SAMPLING SITES:	
Site 1: The es-Samra WSP influent	13
Site 2: WSP effluent	13
Site 3: Al-Tillawi bridge	14
Site 4: Al-Hashmeyeh bridge	14
Site 5: Wastewater pipeline siphon.	15
Site 6: After mixing with the tributary.	15
Site 7: Odwan bridge.	16
Site 8: Jerash bridge.	16
Site 9: King Talal Dam inlet.	17
Site 10: The Al-Sukhneh tributary.	17
 FIGURE 2.1: Typical dissolved oxygen sag for a polluted stream.	 49
 FIGURE 3.1: Location of sampling sites along the River Zarka.	 69
FIGURE 3.2: Nitrate calibration curve for the determination of nitrate.	73
FIGURE 3.3: Nitrite determination calibration curve	73
FIGURE 3.4: Ammonium ion determination calibration curve.	74
FIGURE 3.5: Layout of fermenters used in laboratory batch experiments.	83
 FIGURE 4.1: Temperature and pH variation along the river.	 92
FIGURE 4.2: Dissolved oxygen variation along the river.	93
FIGURE 4.3: Nitrate, nitrite and ammonium concentration variation along the river.	95
FIGURE 4.4: On-site deoxygenation rate at sites 2, 5, and 6.	95
FIGURE 4.5: Orthophosphate variation along the river.	96
FIGURE 4.6: Variation of chloride along the river.	97
FIGURE 4.7: Variation of TOC, BOD and COD along the river.	98
FIGURE 4.8: BOD ₅ and ultimate BOD at different sites along the river.	99
FIGURE 4.9: BOD ₅ , CBOD and NBOD at sites 2 (plant's effluent) and 6 (after mixing with the tributary).	101
FIGURE 4.10: Variation of turbidity along the river.	101
FIGURE 4.11: Hydrogen sulphide variation along the river.	102
FIGURE 4.12: Chlorophyll "a" concentration variation along the river.	103
FIGURE 4.13: Concentration of total bacterial count, <i>Nitrosomonas</i> <i>europaea</i> , <i>Nitrobacter winogradskyi</i> and anaerobic bacteria.	105
FIGURE 4.14: Flow rates of River Zarka and its tributary over the study period.	105
FIGURE 4.15: Quality of River Zarka compared to the quality of the tributary in terms of BOD ₅ over the study period.	106

FIGURE 5.1: <i>Pseudomonas fluorescens</i> exposed to different concentrations of nitrate at an oxygen concentration of 4-6 mg/l and 25°C.	110
FIGURE 5.2: Changes in N-compounds by <i>Nitrosomonas europaea</i> pure culture at 25°C without forced aeration.	111
FIGURE 5.3: Changes in N-compounds by <i>Nitrobacter winogradskyi</i> pure culture at 25°C without forced aeration.	111
FIGURE 5.4: Changes in N-compounds by a mixed culture of <i>Nitrosomonas europaea</i> and <i>Nitrobacter winogradskyi</i> at 25°C without forced aeration.	112
FIGURE 5.5: <i>Pseudomonas fluorescens</i> growth curve in media containing different nitrate concentrations at 25°C without forced aeration.	114
FIGURE 5.6: <i>Pseudomonas fluorescens</i> growth curve in nutrient broth medium and in a prepared medium containing nitrogen concentrations of the Zarka.	114
FIGURE 5.7: Nitrate production in an AS effluent seeded with Zarka N-concentration and aerated with different oxygen concentrations at 25°C.	116
FIGURE 5.8: Nitrite production in an AS effluent seeded with Zarka N-concentrations and aerated with different oxygen concentrations at 25°C.	116
FIGURE 5.9: Ammonium decay in an AS effluent seeded with Zarka N-concentrations and aerated with different oxygen concentrations at 25°C.	116
FIGURE 5.10: Production of nitrate in an AS effluent incubated aerobically and exposed to different nitrate concentrations at 25°C.	119
FIGURE 5.11.a: Nitrate production of an AS effluent incubated anaerobically and exposed to different nitrate concentrations at 25°C.	120
FIGURE 5.11.b: Ammonium accumulation of an AS effluent incubated anaerobically and exposed to different nitrate concentrations at 25°C.	121
FIGURE 5.12: Ammonium decay of an AS effluent exposed to an addition of 25 and 50 mg/l ammonium concentrations at different temperatures.	122
FIGURE 5.13: Ammonium decay in an AS effluent exposed to an addition of 100 mg/l ammonium at different temperatures compared to the original sample.	122
FIGURE 5.14: Nitrate production of an AS effluent exposed to an addition of 100mg/l ammonium at different temperatures compared to the original sample.	122
FIGURE 5.15: Production of nitrate of AS effluent at different cell concentrations at 25°C.	125
FIGURE 5.16: Changes in nitrite concentration of AS effluent at different cell concentrations at 25°C.	125

LIST OF FIGURES (continue)

FIGURE 5.17: Ammonium decay of AS effluent at different cell concentrations at 25°C.	125
FIGURE 5.18: Nitrate production of the Zarka water at different temperatures at site 2.	128
FIGURE 5.19: Nitrite change of the Zarka at different temperatures at site 2.	128
FIGURE 5.20: Ammonium decay of the Zarka at different temperatures at site 2.	128
FIGURE 5.21: Deoxygenation at site 6 of the Zarka for un-aerated sample at different temperatures.	131
FIGURE 5.22: Nitrate production of the Zarka at site 5 at different cell concentrations at 25 °C.	133
FIGURE 5.23: Nitrite change of the Zarka at site-5 at different cell concentrations at 25 °C.	133
FIGURE 5.24: Ammonium decay of the Zarka at site 5 at different cell concentrations at 25 °C.	134
FIGURE 5.25.a: Nitrate production rate of the River Zarka related to cell concentration as measured and modelled by a Monod and a modified power law models.	138
FIGURE 5.25.b: Ammonium decay rate of River Zarka related to cell concentration as measured and modelled by a Monod type and a modified power law models.	138
FIGURE 5.25.c: Nitrate production rate of the AS related to cell concentration as measured and modelled by a Monod and a modified power law type models.	142
FIGURE 5.25.d: Ammonium decay rate of AS related to cell concentration as measured and modelled by a Monod and a modified power type models.	142
FIGURE 5.26: Nitrate production under light and in the dark at different sites at 25°C.	145
FIGURE 5.27: Nitrite change under light and in the dark at different sites at 25°C.	145
FIGURE 5.28: Ammonium decay under light and in the dark at different sites at 25 °C.	145
FIGURE 5.29: <i>In-situ</i> deoxygenation at different sites under light or dark.	146
FIGURE 5.30: Diurnal temperature variation at selected sites of River Zarka.	149
FIGURE 5.31: Diurnal dissolved oxygen variation at selected sites of River Zarka.	149
FIGURE 5.32: Chlorophyll "a" versus algal activity represented by the difference between minimum and maximum diurnal DO along the river.	150
FIGURE 5.33: Diurnal dissolved oxygen of the tributary compared to the Zarka before and after confluence.	151
FIGURE 5.34: Weight of sediment at each site along the river.	153

LIST OF FIGURES (continue)

FIGURE 5.35: Nitrate production at selected sites along the river in the presence of light and with or without river sediment.	154
FIGURE 5.36: Nitrite change at selected sites along the river in the presence of light and with or without river sediment.	154
FIGURE 5.37: Ammonium decay at selected sites along the river in the presence of light and with or without river sediment.	154
FIGURE 5.38: Deoxygenation of river water under light and dark and in the presence and absence of river bed sediment at site 8. . .	155
FIGURE 5.39: Change in nitrate at selected sites along the river placed in light or dark with river sediment.	157
FIGURE 5.40: Change in nitrite at selected sites along the river placed in light or dark with river sediment.	157
FIGURE 5.41: Ammonium decay at selected sites along the river placed in light or dark with river sediment.	157
FIGURE 5.42: Change in nitrate at site 6 aerated with different oxygen concentrations at 25°C.	159
FIGURE 5.43: Change in nitrite at site 6 aerated with different oxygen concentrations at 25°C.	159
FIGURE 5.44: Ammonium decay at site 6 aerated with different oxygen concentrations at 25°C.	160
FIGURE 5.45: Suspended solids concentration along the river (average of 5 runs at off-flood periods) related to weight of sediment.	161
FIGURE 6.1: Simulation flowchart of the two models as applied to the River Zarka.	170
FIGURE 6.2: Measured and simulated BOD of the River Zarka by the Blackwater and Qual 2EU models.	173
FIGURE 6.3: Measured and simulated dissolved oxygen of the River Zarka by the Blackwater and Qual 2EU models.	174
FIGURE 6.4: Measured and simulated ammonium-nitrogen of the River Zarka by the Blackwater and Qual 2EU models.	176
FIGURE 6.5: Measured and simulated nitrate-nitrogen of the River Zarka by the Blackwater and Qual 2EU models.	177
FIGURE 6.6: Flowchart for calculating model coefficients for River Zarka using measured data as inputs and outputs.	178
FIGURE 7.1: Zarka model parameters interaction flowchart.	184
FIGURE 7.2: Measured and simulated Biochemical Oxygen Demand (BOD) by the Zarka and Qual 2EU models.	189
FIGURE 7.3: Ammonium concentration as modelled by the Zarka and Qual 2EU models.	193
FIGURE 7.4: Measured and simulated nitrate concentrations by the Zarka and Qual 2EU models.	195
FIGURE 7.5: Improvement in the DO performance after adopting Scott's (1981) formula for reaeration coefficient under high suspended solids load.	198
FIGURE 7.6: Dissolved oxygen concentration as measured and simulated by the Zarka and Qual 2EU models.	200

LIST OF FIGURES (continue)

FIGURE 7.7: Biochemical Oxygen Demand (BOD) as affected by temperature change using the Zarka model.	203
FIGURE 7.8: Ammonium concentration as modelled at different temperatures by the Zarka model.	204
FIGURE 7.9: Nitrate concentration modelled at different temperatures by the Zarka model.	204
FIGURE 7.10: Dissolved oxygen concentration modelled at different temperatures by the Zarka model.	205
FIGURE 7.11: BOD decay under two hypothetical cases for the Zarka water quality improvement.	210
FIGURE 7.12: Ammonium decay under two hypothetical cases for the Zarka water quality improvement.	210
FIGURE 7.13: Nitrate production under two hypothetical cases for the improvement of the Zarka water quality.	211
FIGURE 7.14: Dissolved oxygen under two hypothetical cases for the improvement of the Zarka water quality.	211

LIST OF TABLES

TABLE 3.1: Geometry of the different sites in summer and winter.	71
TABLE 4.1: Measured quality parameters at all sampling sites along the river (average of 38 samples).	90
TABLE 5.1: Nitrate production and ammonium decay rates of AS effluent at different oxygen concentrations.	118
TABLE 5.2: Ammonium decay and nitrate production rates at different temperatures for different initial ammonium concentrations.	123
TABLE 5.3: Nitrate production and ammonium decay rates at different cell concentrations of AS effluent incubated at 25 °C with 7 mg/l oxygen concentration.	126
TABLE 5.4: Rates of ammonium decay and nitrate production of the River Zarka at different temperatures at selected sites along the river.	129
TABLE 5.5: Nitrate and ammonium rates at 25 °C for different cell concentrations at site 5.	133
TABLE 5.6: Nitrification rates at selected sites along the river under light and dark.	144
TABLE 5.7: Deoxygenation rate along the river under light and dark.	146
TABLE 5.8: Nitrification rates in the presence and absence of river bed sediment along the river under light and dark.	156
TABLE 5.9: Nitrification rate of different water systems at 20°C.	162
TABLE 5.10: Nitrification rates of activated sludge effluent and the Zarka water at different oxygen concentrations.	165

LIST OF TABLES (continue) :

TABLE 6.1: Difference in conditions of the Blackwater, Winooski and Zarka rivers	169
TABLE 6.2: Parameters and coefficients used by the Blackwater model and the Zarka River	179
TABLE 6.3 Coefficients used by the Qual 2EU model and the Zarka river.	179
TABLE 7.1: Data used in Zarka model construction (average of 24 monthly samples):	185
TABLE 7.2: Constants and coefficients for the River Zarka used by the Zarka model.	201
TABLE A1.1: Measured and corrected nitrate and ammonium rates of the River Zarka using both Qual 2EU and Zarka correction factors.	224
TABLE A1.2: Measured and corrected nitrate and ammonium rates of the activated sludge effluent using both Qual 2EU and Zarka correction factors.	225
TABLE A2.1: Site 1 average winter and summer values of tested parameters.	226
TABLE A2.2: Site 2 average winter and summer values of tested parameters.	227
TABLE A2.3: Site 3 average winter and summer values of tested parameters.	228
TABLE A2.4: Site 4 average winter and summer values of tested parameters.	229
TABLE A2.5: Site 5 average winter and summer values of tested parameters.	230
TABLE A2.6: Site 6 average winter and summer values of tested parameters.	231
TABLE A2.7: Site 7 average winter and summer values of tested parameters.	232
TABLE A2.8: Site 8 average winter and summer values of tested parameters.	233
TABLE A2.9: Site 9 average winter and summer values of tested parameters.	234
TABLE A2.10: Site 10 average winter and summer values of tested parameters.	235
TABLE A.3.1: Listing of the mathematical construction used in the simulation of the Zarka model by a Quattro-pro for windows spreadsheets.	236

ACKNOWLEDGMENT:

I would like to express my deepest gratitude to my supervisor Dr. Ashley Scott for his continuous guidance and support over the whole period of my study.

I am indebted to my father for his continuous encouragement and support, to my mother for her warm wishes and blessings, and to my brothers and sisters for their sanctification and encouragement, special thanks are due to Faisal and his family for the warm atmosphere during my stay in England.

My deepest indebtedness goes to my wife Lamia, and to my daughters, Bayan and Diana for their forbearance and patience.

My thanks are extended to the University of Bath, especially to the administration, academic and technical staff of the School of Chemical Engineering.

Last but not least at all, I would like to express my gratitude to the British Council for their financial support during my last year of study.

SUMMARY

A novel approach to a one-dimensional river water quality model is represented in this study. The Zarka model described uses data collected on the River Zarka of Jordan. The river is highly polluted and can be considered to represent semi-treated wastewater effluent, as the prime source is a large waste stabilization treatment plant. The river is characterised by its shallow fast flowing nature, with high loadings of organics and inorganics, along with high bacterial and algal biomass. Conditions of high solar radiation intensities and toxicity inhibited complete nitrification.

The Zarka model focuses on the nitrification process as ammonium concentrations reach 100mg/l at the river's source and nitrate concentrations approach 120mg/l at the river's mouth. The model combines the two important factors affecting nitrification, namely algal and bacterial activity.

Algal activity is represented in the model by the ratio of maximum to minimum oxygen produced in a diurnal cycle rather than its biomass reflected by chlorophyll concentration. The latter proved to be misleading in the River Zarka due to photoinhibition which reduced algal activity but did not significantly affect algal biomass (as regarded by chlorophyll content).

The river is highly responsive to environmental changes, as it is a shallow stream flowing in a semi-arid region. Therefore, as temperature may drop or increase by 10 degrees in a daily cycle, the model is used to predict changes in nitrification within

a range of (5-30°C).

Finally, the Zarka model is used to predict the water quality of the river by adopting two hypothetical cases to improve its water quality. These two cases illustrate that although the river water quality would improve by changing some factors, the prime factor affecting the river water quality is the performance of the treatment plant which is the main continuous source of the Zarka.

CHAPTER ONE

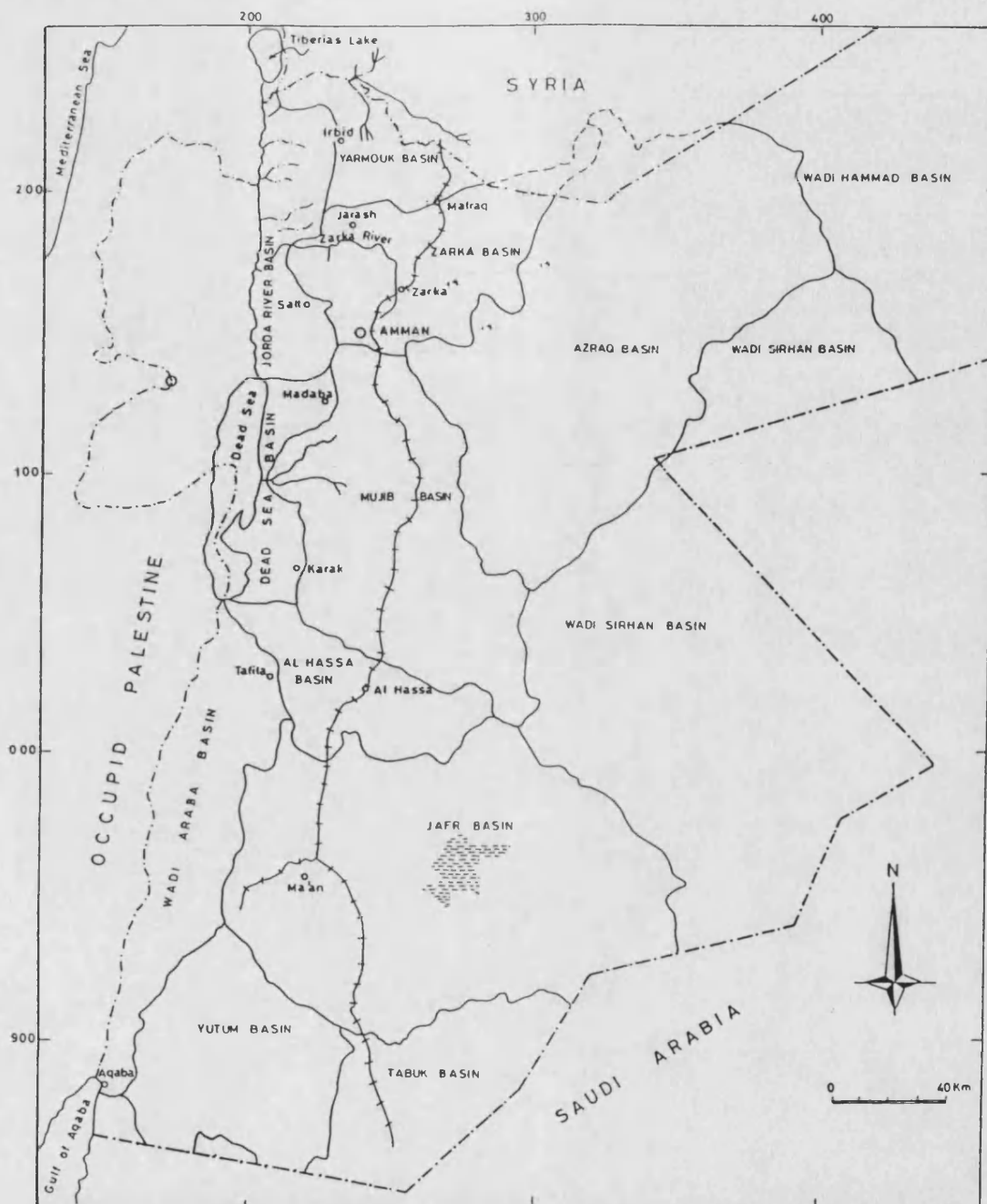
INTRODUCTION

1.1- INTRODUCTION:

Jordan, is a semi arid country, with an annual average rainfall of only 90 mm over the Zarka basin (figure 1.1), and as a consequence suffers from a severe shortage of water. The available water resources, mostly groundwater, are barely enough to meet increasing water demands. Consecutive and frequent population migration waves, over the last three decades, into the country have increased the severity of the problem and hindered proper planning and management of water resources. These resources are either being rapidly depleted due to increasing water demand or polluted due to improper use and management.

The River Zarka is the only continuous flowing surface water stream, from its outfall to its impoundment, that falls completely under the sole jurisdiction of the Jordanian authorities. Other rivers, River Yarmouk and River Jordan, are shared with neighbouring countries, thus planning and management of these rivers are subject to political and international agreements.

The treated wastewater effluent of the esSamra treatment plant has recently become the main source of the River Zarka, (figure 1.2). Its water has been proved to be of a low quality and only useful for restricted irrigation. The river flows through Wadi Dhuleil until it is impounded by the King Talal Dam, the biggest dam in the country. The water collected in this dam is used to irrigate the most fertile part of the country, which produces 60-70% of the country's vegetable products.



LEGEND:
 ++++++ Railway,
 - . - . - . Country boundary
 ——— Basin boundary
 ——— River or waterway

FIGURE 1.1: Surface water basins in Jordan

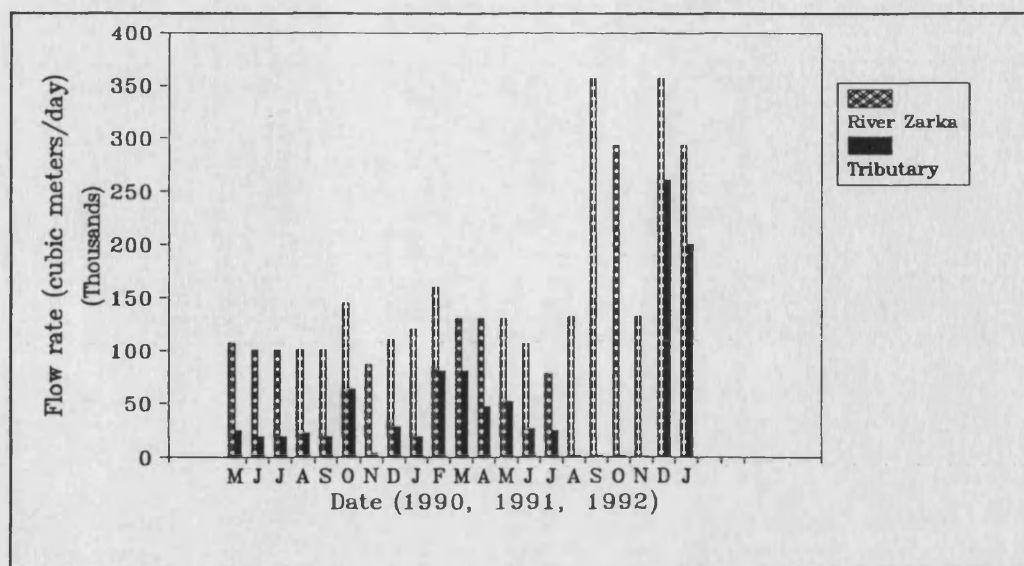


FIGURE 1.2: Flow rates of the Zarka river and the tributary (Al-Sukhneh stream).

If the quality of the river remains the same as at present, all groundwater resources along the river course will get polluted and the fertile soil will get salinized and sterile. There is therefore a clear need for a proper management of this valuable resource.

This study, as a contribution towards the solution of the problem, focuses on nitrification which has recently acquired increasing attention due to its important role in decreasing the toxicity of high nitrogen containing waters. The esSamra treatment plant does not take this process into consideration, since the concentration of ammonium in the influent waters is more or less the same as in the effluent waters.

1.2- THE RIVER ZARKA SYSTEM:

The Amman-Zarka area is inhabited by about 2.2 million people (with a population growth rate of 3.7%/yr), and houses about 90% of Jordan's light to medium industries. As a result, treated, semi-treated, and totally untreated domestic and industrial wastewater enter the water course, (Hashwa, 1985).

The River Zarka, with an average base-flow of 80,000 m³/day in the dry periods, is an essential water source for the country. Although, the river is relatively small, its water is the main continuous source to the King Talal Dam (KTD), the biggest in the country. In turn, after being mixed with other fresh water resources, the dam's water is used to irrigate the Jordan Valley, the most productive agricultural part of the country.

Before 1985, the River Zarka was a fresh water stream originating from springs and wells located upstream. Wastewater used to be treated in a conventional activated sludge treatment plant (Ain Ghazal wastewater treatment plant), until it became quantitatively and qualitatively overloaded due to unplanned population growth. The decision, at that time, was to construct another treatment plant to meet increasing treatment demands.

In 1985, the esSamra plant, the largest wastewater plant in the Middle East, was constructed to serve the capital Amman, Zarka city, and Rusiefeh town. Since that time, the fresh water has been used to serve the domestic requirements of the area, leaving the river with only the treated wastewater of esSamra plant with a different quality, (figure 1.3).

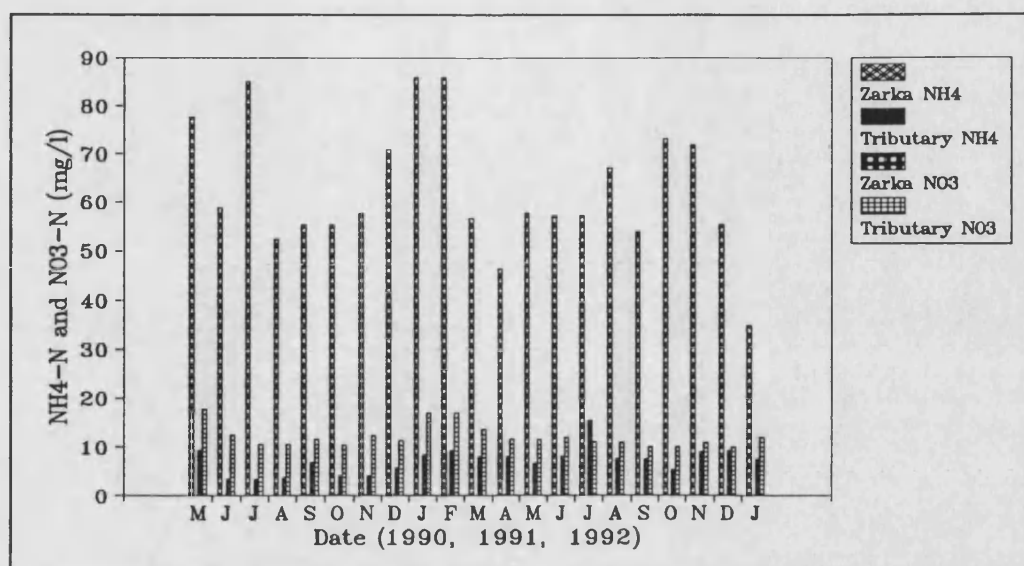


FIGURE 1.3: Nitrate and ammonium concentrations in the Zarka and its tributary.

Saidam (1988) has reported that wastewater flows by gravity through a 39 Km siphon to stabilization ponds at Khirbet esSamra, north east of Amman. Another source of wastewater, domestic as well as some industrial, is also pumped through the siphon to the ponds at esSamra from the second largest city in Jordan, the city of Zarka.

The waste stabilization ponds of the esSamra plant with a total area of 181 ha, consist of three parallel trains, each a series of ten ponds; two anaerobic, four facultative and four maturation. The waste treatment plant uses the waste stabilization ponds as a natural treatment process, due to the availability of land. However, the effluent, hence the river water, has been proved to be of low quality during the last few years, (Salameh and Rimawi, 1987).

The treatment plant is overloaded quantitatively and qualitatively (Saidam, 1988, and Abumoghli, 1991 and 1992). Furthermore, the quality of the effluent is accepted, in other countries, as only of a standard suitable as influent to secondary treatment plants

(Bino 1990).

After a retention period of approximately 40 days in the esSamra stabilization ponds, the effluent is discharged into Wadi Dhuleil. It meets with the Sukhneh tributary (figure 1.4) at a point about 15 km downstream of the plant's outlet, (figure 1.4, point I). The combined streams flow through a natural earthen route until it is impounded at a point approximately 40 km downstream in the King Talal Dam, (Figure 1.4, point IV).

The River Zarka system is a complex one due to the quantity and quality variations of water, much of which are not yet fully identified. This is due to many agricultural and industrial activities taking place along its route. Besides the effluent of the esSamra plant, the river receives effluent from other small treatment plants. These include the Abu-Nuseir plant, which discharges its effluent a short distance from the Odwan bridge, (figure 1.4, point III), and also the Jarash treatment plant effluent, and untreated effluent from a refugee camp, (figure 1.4, point IV). The latter two are being discharged to the river two kilometres before the Jarash bridge. Some photos of the river at the different sites can be seen at the end of chapter one.

Studies on the KTD and its main influent, the River Zarka, have investigated the chemical, physical and biological quality of the water (Hashwa, 1985; Hashwa and Marzolf, 1987; and Salameh *et al.*, 1987). However, no studies on the nitrogen and nitrogen-related processes have yet been carried out on a comprehensive scale and indeed no modelling of the River has ever been attempted. Khoury (1986), has studied

the microorganisms transformation processes of nitrogen compounds in the waters of the KTD taking downstream of the River Zarka as the key source to the dam's water.

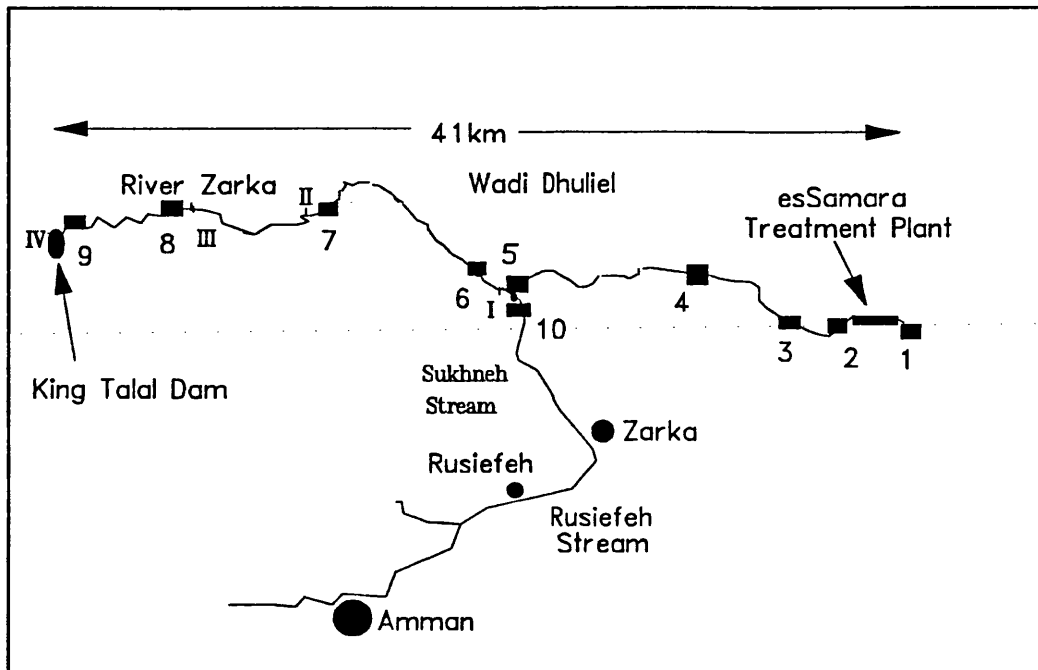


FIGURE 1.4: River Zarka in Jordan

1.3- IMPORTANCE OF NITRIFICATION:

Nitrogen is an important constituent of all living matter. Nitrogen gas constitutes the major fraction in air, yet nitrogen can be a pollutant owing to some of the undesirable effects it can create under certain conditions. Some nitrogen compounds can place considerable demand on the oxygen resources of water bodies, (nitrogenous BOD), and can lead to eutrophication in natural bodies, and in the ammonia form, may be directly toxic to fish, (Arceivala, 1981). The chemistry of nitrogen is complex because of the several oxidation states that nitrogen can assume, and the fact that transformations can occur from one state to another.

The major reactions in nitrogen transformations are:

(1) assimilation of NH_3 and NO_3^- to organic nitrogen,

- (2) occurrence of ammonification when organic nitrogen is converted back to NH_3 ,
- (3) nitrification from NH_4^+ to NO_3^- ,
- (4) denitrification from NO_3^- to N_2 , and
- (5) nitrogen fixation in which molecular nitrogen is reduced to ammonia and then to organic nitrogen, (Arceivala, 1981).

The importance of nitrification lies in producing an oxidized form of N which can participate in denitrification, permitting a potential loss of N from the system.

The biological nature of nitrification was first realized over a hundred years ago when it was shown that the appearance of NO_3^- in soils and sewage was inhibited by antiseptics. It has been established that there were two distinct and separate groups of obligately aerobic bacteria involved (*Nitrosomonas* and *Nitrobacter*), both capable of obtaining energy at the expense of different N compounds, (Grant and Long, 1981).

A consecutive reaction can be used to describe the bacterial nitrification of ammonia. Here, ammonia is oxidized by *Nitrosomonas europaea* bacteria to nitrite, which is often oxidized in a second step by *Nitrobacter winogradskyi* bacteria to nitrate, as indicated by the following sequence, (Shima, Delebeque and Adachi, 1978):



These organisms are mainly chemoautotrophs using CO_2 as a source of carbon, and

are also chemolithotrophs, deriving their energy from redox reactions. Oxidation is essential for their growth. Some heterotrophs may also be involved, (Arceivala, 1981; and Carpenter and Capone, 1983).

When the end products of nitrate reduction are gases, e.g., N_2 and N_2O , the process is called denitrification, because they are ultimately lost to the atmosphere, (Carpenter *et al.*, 1983). Denitrification is an energy-yielding metabolic process that occurs in conditions close to anoxia and that can be carried out by a great number of widely distributed bacteria. This process, extremely important in biological, geochemical and ecological terms, consists of the reduction of ionic oxides of nitrogen (nitrate and nitrite) to gaseous oxides, such as nitrous oxides or molecular nitrogen, (Muela, Gorostiza, Iriberri and Egea, 1988).

1.4- MATHEMATICAL MODELLING:

An important technical element in addressing water pollution impact is the prediction of the effects of various activities, with these predictions being based on appropriate calculations. Calculations can range from the use of mass balance approaches to sophisticated computer models. River quality models are perhaps most usefully applied in long-term planning to maintain or improve the quality of rivers and also in the daily management of river quality, (Knowles and Wakeford, 1978).

Several mathematical models of nitrification have been proposed (Blackwater, Qual I, Qual II, Qual 2EU, and others). Such models can be used to predict nitrifier biomass, growth rates, and concentrations of NH_4^+ , NO_3^- , and NO_2^- under different conditions of NH_4^+ loadings, and at different temperatures and oxygen concentrations.

This kind of modelling can be of great practical value in designing sewage treatment plants, and can also be useful in the prediction of nitrifier response to NH_4^+ fertilizer applications, (Grant *et al.*, 1981).

Nitrification models can be conveniently divided into those that describe planktonic nitrification and those that describe benthic nitrification. Planktonic nitrification models are more appropriate for deep, sluggish rivers. Benthic nitrification models are more likely to be appropriate for shallow rivers, (Cooper, 1986).

1.5- STUDY OBJECTIVES:

The present study was undertaken to investigate the transformation processes (namely, nitrification and denitrification) of nitrogen compounds in the River Zarka by developing a mathematical model that describes these processes. This was achieved by studying the following points:

- 1- The concentrations of the different nitrogen compounds, NH_4^+ , NO_2^- and NO_3^- , from different locations and in different seasons along the course of the river.
- 2- The bacterial population contribution to both processes, nitrification and denitrification.
- 3- The algal biomass and activity effect on nitrification.
- 4- The main factors affecting these processes, such as pH, salinity, algal growth, temperature, substrate loadings, oxygen concentrations, turbidity, light, cell concentration and different carbon sources.
- 5- Laboratory and field batch experiments of both processes on samples taken from different sites of the river course to determine rates, coefficients and

constants of relative parameters.

6- Pure culture studies of the relevant microorganisms.

7- Wastewater effluent studies from other system, activated sludge.

1.6- CONCLUSIONS:

Considering all the above, this study was started to monitor the water quality of the River Zarka concentrating on the nitrogenous compounds. The study was then developed to design a deterministic water quality model to help in understanding the present situation and planning for the future. However, during the process of model development, it was realized that the river is of a unique nature. Consequently, other models could not be applied to describe the River Zarka as proved by the application of two well known models (Blackwater and Qual 2EU). Moreover, the unique quality of the river, did hinder the development of a general model that can be applied to other rivers. However, the Zarka model may be applied to similar systems of similar water quality falling under similar conditions. Although, the designed model in this study forms a solid base for future model development to serve the unique quality of the Zarka and similar systems. The limited time and facilities which were allowed for this study inhibited considering some important factors that affected the river quality and the formulation of the model, i.e. photoinhibition and water toxicity. However, this model constitutes a major part of any future attempt.

Two major deterministic river water quality models have been used in this study to assess the water quality of the River Zarka and have both served to show the inadequacy of existing models in describing a system such as the Zarka. However, they did serve as a guide to the proposed model design. These models are the

Blackwater and the Qual 2EU models, as they are regarded as among the most important. In this study the Blackwater model uses the River Blackwater, England in the application (Casapieri *et al.* 1978) and the Qual 2EU model uses the River Lower Winooski, United States of America (Van-Benschoten and Walter, 1984).

The novel nature of the Zarka model developed in this study stems from the fact that it is the first time that algal and bacterial activities are combined in one model to simulate a river system. Furthermore, the algal activity in terms of oxygen production is used for the first time rather than using algal biomass which proved to be misleading as in the case of the River Zarka.



Site 1: The es-Samra WSP influent



Site 2: WSP effluent



Site 3: Al-Tillawi bridge



Site 4: Al-Hashmeyeh bridge



Site 5: Wastewater pipeline siphon.



Site 6: After mixing with the tributary.



Site 7: Odwan bridge.



Site 8: Jerash bridge.



Site 9: King Talal Dam inlet.



Site 10: The Al-Sukhneh tributary.

CHAPTER TWO

LITERATURE REVIEW

2.1- INTRODUCTION:

By the late 1920s, the basic transformations of the marine nitrogen cycle were fairly well described, (Sutton, Bridle, and Bedford, 1981), although the microbial populations responsible and their locations were still a matter of some dispute. Pioneering work by Waksman and co-workers suggested that marine nitrifying activity was primarily confined to the sediments rather than the water column, (Carpenter, *et al.*, 1983).

Dissolved nitrogen gas in the ocean is about 30 times more abundant than the sum of its inorganic forms (ammonium, nitrite, or nitrate). However, gaseous molecular nitrogen is relatively inert and must be converted into more readily available forms (NH_4^+ , NO_2^- , NO_3^-) before it can be used by organisms, (Carpenter *et al.*, 1983).

Pollutants discharged to a water resource system from domestic sewers, storm water discharges, industrial waste discharges, agricultural runoff and other sources, all of which may be untreated, or inefficiently treated, can have significant effect of both short term and long term duration on the quality of a river system, (Al-Layla, and Al-Rizzo, 1989). Furthermore, discharges of secondary effluent into receiving streams with minimal dilution ratios cause unacceptable degradation of water quality, (Kennedy and Bell, 1986).

The presence and effect of nitrogenous substances in wastewater discharges began to attract attention in the early 1960s in the U.S., and indeed earlier in other places,

primarily because of the role of nitrogen in the eutrophication of receiving waters, (Gee, Suidan, and Pfeffer 1990 (a) and (b)). Ammonia when present with phosphorous, can stimulate undesirable aquatic growth, especially as a function of pH (Keenan *et al.*, 1979), that causes the eutrophication of natural waters, (Rozich and Castens, 1986; Keenan *et al.*, 1979; and Prosser, 1990).

Despite the fact that most of the work has been concentrated on marine water, fresh water has also received some attention. The adverse impact associated with the presence of high concentrations of ammonia and other nitrogenous compounds in fresh water are:

- the reduction in the suitability of that water for industrial reuse due to corrosion and biological growth in cooling-tower and distribution structures, (Gee *et al.*, 1990 a and b)
- production of nitrous and nitric oxides, (Prosser, 1990),
- the presence of ammonia-nitrogen is toxic to fish,
- increases the depletion of dissolved oxygen in receiving streams concomitant with the oxidation of ammonia to nitrate, (Keenan *et al.*, 1979),
- the reduction of chloride disinfection efficiency, (Gee, *et al.*, 1990).
Interference with chlorination due to reactions leads to the formation of chloramine, (Keenan *et al.* 1979).

Nitrogen transformations in aquatic ecosystems are complex and mainly are poorly understood. An overall change in content of nitrogen species can result from various forms of biological activity, namely assimilation of NH_4^+ , NO_2^- and NO_3^- by both

autotrophic and heterotrophic microorganisms, reduction of nitrate and nitrite by denitrifying bacteria, fixation of atmospheric N_2 by algae and bacteria, production of ammonia by deamination of cell organic nitrogen, (Curtis, Durrant and Harman, 1975). Of these processes, it is likely that in flowing oxygenated water, both fresh and polluted waters, nitrification is the most important process.

In addition to nitrification there are many other physical and biological factors affecting water quality. Among the environmental effects of pollution, one of the most crucial is oxygen consumption due to aerobic bacterial activity on organic matter, (Arceivala, 1981). The effects of photosynthesis, denitrification, sedimentation, diffusion, etc., can not be disregarded. But it also seems reasonable to suppose, in some cases, that the nitrification process is related to low DO concentration as observed in the Seine, (Shima *et al.*, 1978).

River quality models are perhaps most usefully applied in long term planning to maintain or improve the quality of rivers, and also in the daily management of river quality, (Knowles *et al.*, 1978). In the past ten years considerable effort has been expended in the development and application of mathematical models for the prediction of water quality of lakes or streams. This effort hopefully was to produce a universal model that could be used on any river or lake, sometimes with calibration, to predict quantitatively the consequences of increased pollutional load on water quality or preferably to indicate how to improve water quality with the implementation of abatement technology. Unfortunately, no such universal model has been successfully developed, (Sandoval, Verhoff and Cahill, 1985; and Grenney, Teuscher

and Dixon, 1978).

In this study, the available water quality models were studied and reviewed in order to have an overall understanding of these models, and to point out areas of inadequate representation of a river like the Zarka.

2.2- NITRIFICATION:

In recent years nitrification has become a standard and widely used wastewater treatment process, (Keenan *et al.*, 1979). Nitrification of sewage treatment prevents discharge of toxic levels of ammonium and, with denitrification, enables removal of nitrogen, reducing the risk of eutrophication, (Prosser, 1990). There has been an increased interest in the role of nitrification in river systems. A primary reason for this has been a general belief that significant nitrification occurs in most rivers to some degree and can, under certain conditions, play a dominant role in affecting the dissolved oxygen status of a river, (Tze-Win and Harold, 1980; and Wild, Sawyer and McMahon, 1971).

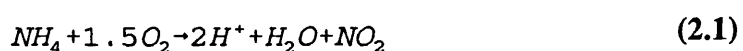
The dearth of reports on nitrification in rivers is due in part to the exceedingly complex nature of the nitrogen cycle in natural water and lack of commonly accepted methods of investigation, (Dunnette and Avedovech, 1983).

Dunnette *et al.* (1983), reported that nitrification is a surface active phenomena, i.e. nitrifying activity of the principal associated organisms, *Nitrosomonas europaea* and *Nitrobacter winogradskyi*, is dependent to a great extent on surface area available for attachment of organisms. Huang and Hopson (1974), also indicated that nitrification

is dependent on biological phenomena, and essentially independent of physical processes.

Nitrification is economically important, especially in polluted waters where ammonia discharge from inadequately treated effluent can constitute both a toxicity problem and, by its oxidative removal, a major factor in the biochemical oxygen demand of the water, (Curtis *et al.*, 1975). Moreover, nitrification can lead to significant losses of ammonia-based fertilizers and subsequently to nitrate pollution of groundwater, particularly in areas of intensive agriculture, (Dunnette *et al.*, 1983).

Nitrification process may be considered in two steps; (Sandoval *et al.*, 1985; Gee *et al.*, 1990; Grant *et al.*, 1981; and Thomann *et al.*, 1987). Ammonia is oxidized under aerobic conditions to nitrite by bacteria of the genus *Nitrosomonas europaea* as follows,:



This reaction requires 3.43 g of oxygen utilization for 1 g of nitrogen oxidized to nitrite. The nitrite thus formed is subsequently oxidized to nitrate by bacteria of the genus *Nitrobacter winogradskyi* as follows:

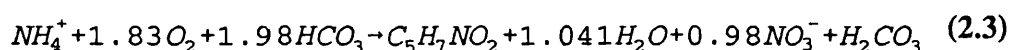


The reaction requires 1.14 g of oxygen utilization for 1 g of nitrite nitrogen oxidized to nitrate. The total oxygen utilization in the entire forward nitrification process is therefore 4.57 g of oxygen per g of ammonia nitrogen oxidized to nitrate. *Nitrobacter winogradskyi* bacteria use about three times as much substrate as *Nitrosomonas*

europaea bacteria to derive the same amount of energy, (Keenan *et al.* 1979; and Courchain, 1962). Actually, some of the ammonium may be used in cell production so that the oxygen utilization may be less than 4.57 and approach 4.2 g O₂/gNH₃ oxidized (Thomann *et al.*, 1987). The process is optimal at mesophyllic temperatures, i.e. 25-35°C, which is similar to Zarka, and slightly alkaline pH, i.e. 7.5-8.0, (Curtis *et al.*, 1975; and Prosser 1986), which is also similar to Zarka.

Nitrite (NO₂⁻) concentrations are generally low in wastewater undergoing nitrification. This is because conversion of NO₂⁻ to NO₃⁻ is rapid compared to the conversion rate from NH₄⁺ to NO₂⁻. In other words, the latter is rate limiting, (Arceivala, 1981).

A stoichiometric relationship can be written for the overall synthesis of biomass and oxidation of ammonia and nitrate as follows.



Nitrifying bacterial biomass can be represented as C₅H₇NO₂ which indicates a theoretical yield of 0.16g biomass per g NH₄⁺-N completely oxidized, (Keenan *et al.*, 1979).

In a study carried out by Gee and co-workers (1990 (a) and (b)) the oxidation of ammonia to nitrate was treated as a one-step oxidation reaction, on the assumption that the first step is rate limiting, (Keenan *et al.* 1979). However, nitrite accumulation has been observed in some processes, indicating that there are conditions where ammonia oxidation may not be rate limiting. Consequently, it is necessary for a better

understanding of the nitrification process to regard it as a two-step reaction, (Gee *et al.*, 1990).

Sufficient affirmative evidence of nitrification would consist of the disappearance of ammonium, slight nitrite build-up, and nitrate build-up with distance from the outfall. This sequence occurs predictably when ammonium-containing river water is incubated in the batch mode, but has rarely been observed in the rivers themselves, (US Department of Commerce, 1977; and Fair *et al.*, 1971). The exceptions are certain rocky-bottomed, usually shallow, receiving streams (like River Zarka), having distinct recovery zones free of additional point source inputs, (US Department of Commerce, 1977).

2.3- DENITRIFICATION

Denitrification is extremely important in ecological and geochemical terms, (Joint Committee, 1977; Arceivala, 1981; and Nakajima, 1981):

- it is the route of formation of almost all atmospheric molecular nitrogen (N_2),
- it is responsible for major losses of nitrogenous fertilizers,
- it is the most feasible means of reducing the content of fixed nitrogen effluent of sewage treatment plants,
- it reduces the dangers of eutrophication in the receiving waters,
- it provides the route by which fixed nitrogen leached from the soil to the ocean is recycled through atmospheric molecular nitrogen to become available to the land masses again by means of nitrogen fixation.

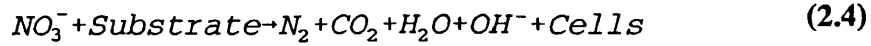
Moreover, one of the by-products of the denitrification process, nitrous oxide (N_2O),

is becoming a source of increasing concern. Nitrous oxide generated in the lower atmosphere diffuses upward into the stratosphere, where it breaks down to form nitric oxide (NO) in a photochemical reaction. Nitric oxide reacts with ozone, leading to the destruction of the major barrier protecting the living organisms from ultraviolet radiation, (Mortimer *et al.* 1981).

Denitrification is an energy-yielding metabolic process that occurs in conditions close to anoxia (absence of molecular oxygen). The influence of oxygen on denitrification is important and controls the process by a) oxygen competing with nitrate for electron donors, and b) oxygen inhibiting the synthesis of enzymes catalysing denitrification. Although oxygen is consumed in nitrification, that from the nitrate form remains available for use when free dissolved oxygen is depleted and denitrification continues to occur, (Arceivala, 1981).

Denitrification can be carried out by a great number of widely distributed heterotrophic microorganisms that utilize nitrate as a hydrogen acceptor (when an organic energy source is available) and involves the transfer of electrons to the nitrate reducing enzyme via cytochromes, (Dodd and Bone, 1975). This process comprises the reduction of ionic oxides of nitrogen, nitrate and nitrite, to gaseous oxides such as nitrous oxides or molecular nitrogen, (Muela *et al.*, 1988; and Grant *et al.*, 1981).

Denitrification will also occur under conditions of endogenous respiration, although at a much slower rate, as described by the following equation, (Eckenfelder, 1989):
In the anoxic reaction, the formation of 3.57 mg alkalinity as CaCO_3 for each



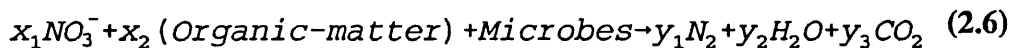
milligram of NO_3 -N denitrified is predicted. This amounts to one-half of the alkalinity that is consumed during nitrification. Most of this alkalinity, however, is lost by reaction with CO_2 generated. Approximately 3 mg/l of BOD is consumed for each mg/l of NO_x -N reduced, (Eckenfelder, 1989; and Joint Committee, 1977).

The pathway of denitrification is as follows:



Nitrite and N_2O are generally accepted as the obligatory and stable intermediates of denitrification. Evidence for this was provided by transient accumulation of nitrite during nitrate reduction, accumulation of N_2O in the presence of acetylene and ^{15}N -labelling of N_2O and N_2 from $^{15}NO_2^-$ (Carpenter *et al.*, 1983). Although nitrate and nitrite are reduced photochemically, these processes are restricted to the top thin layer of surface water (Hamilton, 1964). Only biological processes are of quantitative importance in the transformation of nitrate in marine environments, (Carpenter *et al.*, 1983).

A simplified denitrification reaction is



Denitrification may vary widely. This could be caused by a number of factors such as the activity of the denitrifier, and the carbon source, which is essential for denitrification and its availability. The carbon source may be internally available in sewage, either in the raw sewage or from endogenous respiration, or artificially added

in different forms, (Arceivala, 1981). One study (Joint Committee, 1977) demonstrated that a C:N ratio of at least 3:1 was necessary after nitrification to promote denitrification. At lower C:N ratios, the rate of denitrification decreased rapidly.

In situ denitrification rate is affected by many factors, e.g., temperature, pH, Eh (oxidation-reduction potential), and concentrations of oxygen, nitrate and organic matter, (Carpenter *et al.*, 1983). These factors are not always independent of each other, and are at times, difficult to control or to simulate throughout assaying processes.

2.4- MODELLING

During the past few years, numerous mathematical models have been applied to simulate water quality conditions in rivers. These models vary considerably in the degree of resolution (refinement) with which they represent the physical world. Low resolution models represent general trends for a few linked dependent variables over a limited set of boundary conditions. High resolution models may be used to represent the responses of a large number of linked dependent variables over a much wider set of boundary conditions, (Grenney *et al.*, 1978). As the order of resolution of a model increases, so does the difficulty and cost of its application. The selection of a model for a particular situation requires value judgements of acceptable trade-offs between the practicability and economy of model application and the amount and refinement of information to be provided by the model responses.

Nitrification models can conveniently be divided into those that describe planktonic and those that describe benthic nitrification. Planktonic nitrification models are more

appropriate for deep, sluggish rivers, depth greater than several meters and velocities less than approximately 0.2 m/s. Benthic nitrification models are more likely to be appropriate for shallow rivers, (Cooper, 1986).

The majority of nitrification models are deterministic, (Sandoval *et al.*, 1985). Deterministic models attempt to simulate the natural processes of self- purification in a river system. Each process is modelled mathematically using derived parameters and rate constants. A deterministic model will predict a unique result from a specified set of input conditions without any consideration of the true relationship between predicted results and inputs. Decisions based on deterministic models should incorporate an evaluation of the errors involved in the utility of the results, (Crabtree, Cluckie, Forster and Crockett, 1986). System behaviour depends on the provision of constants found in the equations and on initial conditions.

The other type of models is the stochastic or probabilistic model which attempts to randomize error by containing one or more random variability of each parameter for each input, (Crabtree *et al.*, 1986). Usually the stochastic approach is less convenient because the relationships between loads and qualities have to be established by data collection and statistical analysis for the particular rivers, while deterministic models could be applied to any river without collection of quality data except a small amount for checking purposes, such as from one or two 24-h sampling surveys, (Knowles *et al.*, 1987). As a consequence, stochastic river models are rare, (Prosser, 1990).

The first deterministic model was proposed by Streeter and Phelps in 1925, as cited

by Sandoval *et al.*, (1985), with two equations predicting the evolution of dissolved oxygen demand, BOD. This model assumed that the BOD decay rate was proportional to BOD, the deoxygenation rate was equal to the BOD decay rate, and the re-oxygenation rate proportional to the oxygen deficit, (Poch *et al.*, 1986). Streeter and Phelps model was described as follows, (Canter, 1988):

$$D_t = k_1 \frac{L_a}{k_2 - k_1} (10^{-k_1 t} - 10^{-k_2 t}) + D_a 10^{-k_2 t} \quad (2.7)$$

where:

D_t = DO deficit at any down-stream flow time t , (day).

k_1 = coefficient of deoxygenation, (day^{-1}).

k_2 = coefficient of reaeration, (day^{-1}).

L_a = BOD_u in the stream following mixing (mg/l).

D_a = DO deficit upstream of waste discharge (mg/l).

The basic concepts behind models of a particular type are similar, and they differ primarily only in their approach to a specific problem. The general rule for the conservation of mass applies to all. This rule is fundamental to the analysis of any water quality problem and describes the relationship between the transport of a substance through a water volume and the sources and sink of mass within it. This equation is derived by writing a mass balance over a differential volume. It is stated by the following equation, taking the water next to the surface as upper waters and that next to the bottom bed as bottom waters, (Sandoval *et. al.*, 1985):

time rate of change of mass element	=	rate of mass in	-	rate of mass out	+	the difference between that produced by the sources and that removed by the sinks
---	---	-----------------------	---	------------------------	---	---

In mathematical terms this equation becomes:

$$\frac{dY}{dt} + U_{(x,t)} \frac{dY}{dx} = S(Y, X, x, t) \dots \dots \dots \text{upper-waters} \quad (2.8)$$

and

$$\frac{dX}{dt} + U_b(x, t) \frac{dX}{dx} = S(Y, X, x, t) \dots \dots \dots \text{bottom-waters} \quad (2.9)$$

where:

Y= concentration of upper (surface) water quality variables, (mg/l)

X= concentration of bottom water quality variables, (mg/l)

S= sources and sinks of the substrate being considered

U= upper velocity of the stream, (m/day)

U_b= bottom velocity of the stream, (m/day)

x= distance downstream, (m)

t= time, (day).

The failure of models in predicting the water quality of a system can stem from:

- 1) model application to a variable or process that is too complex for formulation without quantifying the major parameters and assumptions.
- 2) application of sophisticated general case models without adequate understanding of the particular river in question.
- 3) misapplication of model calibration and verification procedure and
- 4) the use of poor data for interpretation, model calibration and model verification.

To overcome these deficiencies, the selection of a particular model or model configuration should be accompanied by a statement of limitations, predictive accuracy and suggested applications.

Many mathematical models have been derived to describe different systems, the most well known and used are the Blackwater model, (Casapieri *et al.*, 1978) and the Qual 2EU model, (Van-Benschoten *et al.*, 1984). These models are described in sections 2.4.1 and 2.4.2 and discussed in section 2.4.3 and will be used later on (chapter 6) to simulate the River Zarka system in order to highlight the importance of different model parameters.

2.4.1- QUAL 2EU MODEL:

A model which has been widely applied in the past few years is the moderate resolution QUAL II model. The original QUAL I, (Grenny *et al.*, 1978) was developed by the Texas Water Development Board (TWDB) to simulate conservative constituents, temperature, biochemical oxygen demand, and DO in a one dimensional steady flow river. The U. S. Environmental Protection Agency (EPA) developed the model by adding additional constituents (ammonia, nitrate, coliform, phosphate and algae). The resulting model is generally referred to as QUAL II, although a number of different versions now exist, (Grenney *et al.*, 1978; and Al-Layla *et al.*, 1989).

Qual-II is applicable to well mixed streams and predicts both the temporal and spatial variations of up to 13 water quality constituents. These are: temperature, DO, BOD, algae (chlorophyll-a), phosphate, ammonia, nitrate, nitrite, coliform, an arbitrary non-conservative substance and up to 3 conservative substances, (Crabtree *et al.*, 1986).

QUAL II is perhaps the most comprehensive in a group of water quality models in use in the United States. It is readily adaptable to a wide variety of river quality modelling situations and has been modified for use on major European river systems, e.g. Blackwater, Loddon, and Seine, (Kuchenrither *et al.*, 1983).

The model numerically solves the one-dimensional advection dispersion equation for the water quality variables. The equation represents a differential mass balance on the volume of each computational element in the system. The application of the system contains the following variables, (ncasi, 1980):

a) dissolved oxygen,

$$= F + k_2 (C_{sat} - C) + (\alpha_3 \mu - \alpha_4 \rho) A - k_1 L - \frac{k_4}{A_x} - \alpha_5 \beta_1 N_1 - \alpha_6 \beta_2 N_2 \quad (2.10)$$

This equation contains seven terms which represent oxygen sources and sinks, where;

- 1) The first term "F" is an input forcing function which responds to the environmental and hydrological characteristics specified by the model user.

- 2) The second term is the reaeration from the atmosphere, where;

k_2 = reaeration coefficient, (day^{-1})

C = DO concentration, (mg/l)

C_{sat} = saturation DO concentration, (mg/l)

- 3) The third term is due to respiration of benthos and algae, where;

μ = local specific growth rate of algae, (day^{-1})

ρ = local respiration rate of algae, (day^{-1})

α_3 = benthos source rate for ammonia nitrogen, ($\text{mg/m}^2\text{-day}$)

α_4 = ratio of oxygen uptake per unit of algae respired

A = Algae biomass concentration, (mg/l)

- 4) The fourth term is due to BOD decay, where;

k_1 =rate of change in BOD, (day⁻¹)

L = ultimate BOD concentration in river reach, (mg/l)

- 5) The fifth term is due to sediment oxygen demand, where;

k_4 = rate coefficient for sediment oxygen demand,
(mg/day/m)

A_x = average cross sectional area of computation
element,(m²)

- 6) The sixth term is due to oxidation of ammonia, where;

α_5 = ratio of oxygen uptake per unit of ammonia-N oxidized

β_1 = rate coefficient for the biological oxidation of ammonia,
(day⁻¹)

N_1 = concentration of ammonia-N in river reach, (mg/l)

- 7) The seventh term is due to oxidation of nitrite-N, where;

β_2 = rate coefficient for the oxidation of NO₂-N, (day⁻¹)

N_2 = concentration of NO₂-N in river reach, (mg/l)

α_6 = ratio of oxygen uptake per unit of NO₂-N oxidized.

b) carbonaceous biochemical oxygen demand,

$$=F-k_1L-k_3L \quad (2.11)$$

where:

k_3 = Coefficient for settling and scour effects, (day⁻¹)

L= ultimate BOD concentration, (mg/l).

c) algae as chlorophyll "a",

$$=F+(\mu-\rho+\sigma_1/h)A \quad (2.12)$$

where:

σ_1 = local settling rate of algae and, (m/day)

h= mean depth of flow.

d) ammonia-nitrogen

$$=F+\alpha_1\rho A-\beta_1N_1+\frac{\alpha_3}{A_x} \quad (2.13)$$

e) nitrate nitrogen

$$=F+\beta_2N_2-\alpha_1\mu A \quad (2.14)$$

f) nitrite nitrogen

$$=F+\beta_1N_1-\beta_2N_2 \quad (2.15)$$

The model conceptualizes the stretch of river studied as a series of reaches. Reaches are assumed to represent portions of the river having uniform conditions (geometric, hydraulic and chemical/biological coefficients). Reaches are further subdivided into units called computational elements. Each element is modelled as a constant volume, completely mixed reactor with input, output and reaction terms. The mathematical model contains sub-models covering the quality parameters, determination of coefficients, temperature calibration and hydraulic sub-model.

Application of the Qual II river model in Utah indicated several inherent model limitations, the most significant being flow discontinuities at large diversions, (Grenney *et al.*, 1978). Qual 2EU is also applied to the River Zarka system and will

be discussed later (Chapter 6).

2.4.2- BLACKWATER MODEL:

The River Blackwater model is one-dimensional, deterministic and operates in a steady state mode, although dissolved oxygen changes due to photosynthesis are modelled as non steady state, due to diurnal variations in light intensity, (Crabtree *et al.*, 1985).

The water quality constituents simulated are dissolved oxygen, carbonaceous BOD, ammonia and nitrate. The rate of nitrification is controlled by the concentration of *Nitrosomonas eurpaea* bacteria. The model input requires user calculated hydraulic relation-ships for each reach, for example, depth, time of travel, and channel cross-section. Also, relative plant density for each reach needs to be supplied. The model is based on fieldwork derived rate constants and constants. Mathematical solution is by numerical integration of complete differential equations, (Knowels *et al.*, 1978, Casapieri *et al.*, 1978; and Crabtree *et al.*, 1986).

The determinants used in the simulation of the model are:

a) BOD, rate of loss of BOD due to:

1- oxidation

$$=-k_b [BOD] \text{ mg/l.min} \quad (2.16)$$

where:

k_b is BOD decay constant, (min^{-1}) and

[BOD] is concentration of BOD (mg/l)

2- settling of suspended matter if river velocity < 0.2 (m/s).

$$= -k_s * f_s * [BOD] \quad (2.17)$$

where

k_s = settling rate constant,

f_s = fraction of BOD that is settleable

or if river velocity is > 0.4 (m/s)

$$= R_s * \frac{V^2}{D} \quad (2.18)$$

where

R_s = resuspension rate constant, and

V = river velocity (m/min), and D = river depth (m).

b) Ammonia, rate of loss of ammonia by nitrification, bed consumption, weir, reaeration, demands from BOD and ammonia, plant respiration and photosynthesis, (mg/l.min.).

$$= - \left[\left(\frac{F_6}{A_6} \right) \left(\frac{d(CM)}{dt} \right) \left(A \exp \left((B_n) - 1.7918 \right) \right) \right] * \left[\frac{(W_p) (DO)}{(1000 (AV) ((DO+1)))} \right] * [A] \quad (2.19)$$

where:

$$\frac{dCM}{dt} = F * k * CM * A [(k_s) + A] \quad (2.20)$$

where

A is NH_4-N concentration, (mg/l)

B_n is a value depending on the nature of the bed representing the amount of

Nitrosomonas europaea, range (1-4),

W_p is the length of the wetted perimeter, (width plus twice the depth, m)

F is usually 1.0 and allows modification of growth rate

k is the maximum growth constant for *Nitrosomonas europaea*

K_s is a saturation constant

F_6 is 1.0, and A_6 is 0.05, (equation constants)

AV is the average cross sectional area of the stretch, (m^2)

DO is the dissolved oxygen concentration, (mg/l).

c) Nitrate, incorporating nitrate formation by the oxidation of ammonia and denitrification representing its loss.

$$= - \frac{k_a * k_2 * W_p * CN}{(1440000 * A)} \quad (2.21)$$

where:

k_a is bed type dependent in the range 0.29-3.0, where the lower value represents a clean gravel-type bed which would not support high concentration of denitrifying bacteria.

k_2 is a rate constant given by

$$\log_{10} (K_2) = 0.0293 (T) + 0.0294 \quad (2.22)$$

CN is concentration of NO_3-N , (mg/l)

T = temperature in $^{\circ}C$.

d) Dissolved oxygen

1- due to reaeration

$$= S_p * K_R * \frac{[C_s - C]}{D} \quad (2.23)$$

where:

A_x is the average cross sectional area, (m^2).

S_p is usually 1.0 and allows for conditions of the water surface,

K_R is reaeration constant given by

$$K_R = 1.042^{T-20} (0.508) [(VC) + 0.3406]^{0.67} \frac{(DC)^{-0.85}}{60} \quad (2.24)$$

where:

VC is river velocity (cm/s), and DC river depth (cm),

C_s is air saturation value (mg/l),

C is DO concentration (mg/l),

D is the river depth (m).

2- due to weirs and water falls

$$= \frac{[(RT * C_s) - (C_s + C)]}{RT} \quad (2.25)$$

where:

RT is given by:

$$RT = 1 + 0.11 (AW) * (BW) * H * (1 + 0.046 T) \quad (2.26)$$

in which:

AW=0.64 for sewage effluent,

BW=1.0 for free fall, and

H=height of the water fall (m).

3- due to river bed respiration

$$= -B * A_3 * \frac{C^{B_3}}{D} \quad (2.27)$$

where:

B=1.0, B_3 =0.45 (equation constants)

A_3 is given by

$$A_3 = (A_8) \exp [0.0693 (T-15)] \quad (2.28)$$

where:

$$A_8 = 0.000703$$

4- due to plant respiration

$$= -A_4 * \frac{MC^{0.3}}{D} \quad (2.29)$$

where:

M is the dry density of the plants g/m²,

A₅ = 0.3 (equation constant)

A₄ is given by:

$$A_4 = A_9 \exp (0.0693 (T-15)) \quad (2.30)$$

where:

A₉ = 0.000013 (equation constant)

5- due to photosynthesis

$$= A_1 * \frac{I^{0.79}}{D} \quad (2.31)$$

where:

A₁ is 0.00103 (equation constant),

I is light intensity (cal/cm².hr)

6- due to nitrification

$$= 4.33 * (dA/dt) \quad (2.32)$$

where:

dA/dt is given in equation (2.19) above.

2.4.3- COMPARISON OF THE BLACKWATER AND QUAL 2EU MODELS:

Based on a study carried out by Crabtree *et al.* (1986), they stated that neither model does particularly well at modelling nitrate-nitrogen, the points mentioned below represent the major differences between the two models. Before then, an important point must be mentioned; When considering most of the papers dealing with these models it can be clearly noticed that some of the authors have rewritten the equations in a different manner which largely affects the overall model. For instance, (which is not the only case as will be shown later in chapter 6), Knowles *et al.* (1978) have divided the whole terms of the equations representing the rate of change in dissolved oxygen by the depth, while Crabtree *et al.* (1986) have divided the power in these equations by the depth, i.e.

Rate of change due to river bed respiration:

$$=-B(A_3) * \frac{C^{(B_3)}}{D} \dots \dots \text{Knowles, et-al. (1978)}$$

and

$$=B(A_3) C^{(\frac{B_3}{D})} \dots \dots \text{Crabtree, et.al, (1986)}$$

- 1- The Blackwater model is small and specific while Qual 2EU is large and general purpose model.
- 2- Qual 2EU can represent a whole catchment system including tributaries, while Blackwater model has no way of entering non-point sources which have to be combined and entered as point sources.
- 3- Qual 2EU uses algae as the biological factor affecting DO concentrations while Blackwater uses plant density and *Nitrosomonas europaea* bacteria.

- 4- Blackwater model uses a single nitrification stage controlled by *Nitrosomonas europaea* bacteria, while Qual 2EU uses a two stage nitrification of algal growth to influence the conversion rates from ammonia to nitrite and from nitrite to nitrate.
- 5- Reaeration by weirs cannot be modeled by Qual 2EU without manipulating some coefficients.
- 6- Benthic sources and sinks are not included in the Blackwater model.
- 7- Qual 2EU is limited to the number of elements, reaches, headwaters, junctions and input or withdrawal elements. While the Blackwater model is not limited to number of reaches or input or withdrawal but only one headwater and no junction points.
- 8- Qual 2EU includes longitudinal dispersion, whereas Blackwater does not.
- 9- The temperature is modelled by Qual 2EU, while it is not by the Blackwater.
- 10- Reaeration can be calculated by one of eight equations in the Qual 2EU model, while only one equation is used by the Blackwater model.

Both models will be used to simulate River Zarka in chapter 6 where again some other differences will be mentioned to highlight the reasons behind the need for a special model for the Zarka system which couldn't be successfully represented by either of the two models.

2.5- FACTORS AFFECTING NITRIFICATION:

Essential factors for nitrification are oxygen, phosphates, and an alkaline environment to neutralize the resulting acids like HNO_3 and N_2O , (Thomann *etal.*, 1987). Nitrifying bacteria are very susceptible to the action of toxic substances. Temperature, substrate

concentrations, pH and other factors affect the nitrification and denitrification processes and consequently they should be considered when modelling nitrification. These factors have been studied by many researchers, working under different environments and conditions. The overall result is a dispute about their significance.

2.5.1- BACTERIA:

An understanding of microbial cycling of nutrients in natural ecosystem requires knowledge of both types and numbers of microorganisms involved, and the nature of the processes they carry out. The study of microorganisms in natural environments is, however, notoriously difficult. In particular, the isolation, characterization, and enumeration of typical dominant or significant microbial population is plagued by the lack of reliable *in situ* detection techniques, problems associated with nondestructive removal of cells, and choice of suitable media and cultural conditions for growth in the laboratory. These problems are exacerbated in studies of nitrifying bacteria. As autotrophic ammonia- and nitrite-oxidizing bacteria do not form visible colonies on solid medium, the dilution plate technique is not convenient for routine use, (Prosser, 1990). The length of incubation period is also critical; Matulewich (1975) as cited by Prosser (1990) found that MPN counts of nitrite oxidizers had not reached a maximum after 100 days of incubation. However, many authors have rejected the number of microorganisms as an absolute indicator of activity, (Muela *et al.*, 1988).

Of the total oxygen demand exerted by wastewater, there is often a sizeable fraction representing the amount used for the oxidation of ammonia to nitrate. The autotrophic bacteria *Nitrosomonas eurpaea* and *Nitrobacter winogradskyi* are responsible for this two stage conversion, although other organisms appear to oxidize ammonia under

certain conditions. *Nitrosomonas europaea* and *Nitrobacter winogradskyi* are the types most commonly isolated from soils, sewage, and the freshwater environment, (Grant *et al.*, 1981). Being autotrophic and gram negative, *Nitrobacter winogradskyi* and *Nitrosomonas europaea* must reduce oxidized carbon compounds, such as carbon dioxide and its ionic species, in wastewater for cell growth, (Joint Committee, 1977; and Bergey's manual, 1974). All of the organisms placed in this family are obligate aerobes and none requires organic growth factors.

Curtis *et al.* (1975) reported that *Nitrosomonas europaea* are known to be a slow-growing organisms, (Gee *et al.*, 1990) with mean generation times for a number of strains ranging between 11 and 58 hr. Thus in the most dilute aliquot (theoretically 1 cell ml⁻¹) a considerable incubation time is necessary; for example, in order to detect 0.1 mg NO₂-N, 2*10⁶ cells would take 23 days. Thomann *et al.*, (1987) reported that the generation time of organisms is in the order of one day, by contrast to an order of a few hours for many heterotrophic bacteria. Arceivala (1981) found the generation time to range between 10 and 30 hr depending on temperature, oxygen content of the water, and the initial concentration of nitrifying bacteria, (Poch *et al.*, 1986; and Joint Committee, 1977). The minimum doubling time reported by Prosser (1990) for nitrifying bacteria is 8 hr. Although the rate of growth of nitrifiers is low, these autotrophic microorganisms should physiologically respond to changes in their environment, in a similar manner to heterotrophs, (Shieh and LaMotta, 1979).

It is generally accepted that the specific growth rate of *Nitrobacter winogradskyi* is higher than the growth rate of *Nitrosomonas europaea* and hence there is no

accumulation of nitrite in the process and the growth rate of *Nitrosomonas europaea* will control the overall reaction, (Eckenfelder, 1989). It was also observed that *Nitrobacter winogradskyi* activity was highly dependent on the ratio between *Nitrobacter winogradskyi* and *Nitrosomonas europaea* population. When this ratio was minimal, with only ammonia as the substrate, the specific activity of the *Nitrobacter* was highest. As the ratio of *Nitrobacter winogradskyi* to *Nitrosomonas europaea* increased, when the nitrogen substrate was shifted from ammonia to nitrite, the specific activity of *Nitrobacter winogradskyi* decreased. The specific activity of the *Nitrobacter winogradskyi* was reduced to about one-third of the optimum activity when the *Nitrosomonas europaea* populations was one-tenth of its maximum density. On the other hand, the activity of *Nitrosomonas europaea* was not affected by the ratio of the two groups of nitrifiers, (Gee *et al.*, 1990).

Moreover, nitrification proceeds more rapidly in mixed culture than in pure culture, with the mixed culture much closer to the actual biota in the wastewater treatment facilities, (Huang *et al.*, 1974).

Mortimer *et al.* (1981) indicated that denitrifiers are ubiquitous, and are not necessarily restricted to anaerobic environments containing nitrate or one of the intermediates of its reduction (nitrite, NO, or N₂O). The major group isolated was representative of *Pseudomonas fluorescens*; the second most prevalent group was representative of *Alcaligenes xyloxydans*. While Bergey's (1974) stated that *Pseudomonas fluorescens* are strict aerobes, except for those species which can use denitrification as means of anaerobic respiration.

2.5.2- TEMPERATURE

In general, the rates of chemical and biological reactions increase with temperature. An approximate rule is that the rate of a reaction will about double for each 10°C rise in temperature. In biological reactions, this rule will hold more or less true up to a certain optimum temperature. Above this the rate decreases, probably owing to destruction of enzymes at the higher temperatures, (Sawyer and McCarty, 1978; and Shima *et al.*, 1976).

The temperature of a river varies with time and position. Since the variation of temperature with position is usually small, only the variation with time is normally taken into account; through this variation the parameters affected by temperature are correlated to time. Data found in the literature indicate that temperature exhibits diurnal and annual periodicity, and it is advantageous to fit the data to a sine function with either a one-day cycle or a yearly cycle for respectively a daily or yearly model, (Sandoval *et al.* 1985).

Arceivala (1981) stated that rate constants for BOD removal, bacteria die off, nitrification, and reaeration in streams are all affected by temperature which can shift the minimum DO and its point of occurrence along the river. Nitrifying organisms are also sensitive to temperature. Stream temperatures around 25 to 28°C, as in warmer climates (like Zarka basin area) or where thermal pollution is occurring, are optimum for their growth. The summer temperatures of River Zarka approach 30°C.

Wild *et al.* (1971) reported that the rate of nitrification increased with temperature.

Their study showed that up to five times the detection time may be needed to accomplish complete nitrification in the colder seasons as is needed in the summer.

Parkasam and Loehr (1972) found that an increase in temperature from 25 to 35°C increased denitrification rates. Sheih and Motta (1979); Eckenfelder, 1989; and Peavy, Rowe and Tchobanoglous, (1987) found an optimum temperature between 30 and 35°C, and have been reported as not growing below 14 °C, (Carpenter, 1983).

Dodd *et al.*, (1974) cited the work of Dawson and Murphy (1972) which showed that an Arrhenius temperature relationship holds for the typical mesophyllic denitrifying bacteria *Pseudomonas denitrificans* from 5 to 27 °C and this is probably true for most denitrifiers. Also, Shima *et al.* (1986) used the Arrhenius equation to describe the temperature effect as was also done by Harry *et al.* (1971), Prosser (1990) and Keenan *et al.* (1979).

Wong-Chong *et al.*, (1978) found that the maximum oxidation rate appeared to be independent of temperature but the oxidation rate obeyed Arrhenius law. The Arrhenius equation can be described as:

$$\mu_m = Ae^{-E/RT} \quad (2.33)$$

where:

μ_m = specific oxidation rate,

A = Arrhenius coefficient = 2.175×10^9 , (day⁻¹),

E = activation energy, (cal/mole),

R= the gas constant, and

T= Temperature, (°C).

Similar temperature functions have been used in a number of computer models for sewage treatment, but there are few experimental data on the effect of temperature on growth of pure cultures of nitrifiers.

Prosser (1990) cited the work of Randell *et al.*, (1982) who found that ammonia accumulates at below 10°C, nitrite at between 10 and 16°C, and nitrate at above 16°C due to differences in the relative activities of ammonia oxidizers, nitrite oxidizers and ammonifiers. While Grant *et al.*, (1981) found the accumulation of nitrite to occur at less than 6°C.

However, Wild *et al.* (1971) cited the work of Borchardt (1966) who indicated that the temperature had little effect on nitrification in the range of 15°C to 35°C. Wong-Chong *et al.*, (1978) also reported that the maximum oxidation rate of nitrite is independent of temperature. Furthermore, Alford (1969) confirmed that no temperature effect on reaction could be shown with nitrate reduction.

It is clear that there is a large dispute about the effect of temperature on nitrification rate and on its implementation in a model to describe its effect. However, these differences could be related to the methods used in the detection and the assumptions and simplifications adopted prior to the investigation and more profoundly on the quality of the studied water.

2.5.3- DISSOLVED OXYGEN (DO):

The sources of DO are; (1) reaeration from the atmosphere, (2) photosynthetic oxygen production, and (3) DO in incoming tributaries or effluent. While internal sinks of DO are: (1) oxidation of carbonaceous waste material, (2) oxidation of nitrogenous waste materials, (3) oxygen demand of sediments of a water body, and (4) use of oxygen for respiration by aquatic plants.

The oxygen demand for complete nitrification is high. For most domestic wastewaters, it will increase the requirements for carbonaceous BOD removal by 75 to 100 percent since complete nitrification requires from 4.3 to 4.6 g of oxygen for each g of ammonia nitrogen converted into nitrate, and wastewaters generally contain 20 to 30 mg/l of reduced nitrogen, (Joint Committee, 1977).

Exertion of the BOD results in deoxygenation of receiving waters. Absorption of oxygen from the atmosphere and from green plants during photosynthesis results in re-oxygenation or reaeration. In streams, the interplay between deoxygenation and reaeration produces a dissolved oxygen profile called the oxygen sag, (Gordon *et al.*, 1971). As an engineering concept, the sag curve possesses two characteristic points; (1) a point of maximum deficit, the critical point, and (2) a point of inflection, the point of maximum rate of recovery, (Fair *et al.*, 1971). Figure (2.1) illustrates a typical oxygen sag curve based on that cited by Fair *et al.* (1971) who plotted DO reaeration and deficit versus time of travel along the path of water movement in order to derive reaeration and oxygen utilization rates per time. However, this plot can also be represented in terms of distance if the time of travel between two points is known.

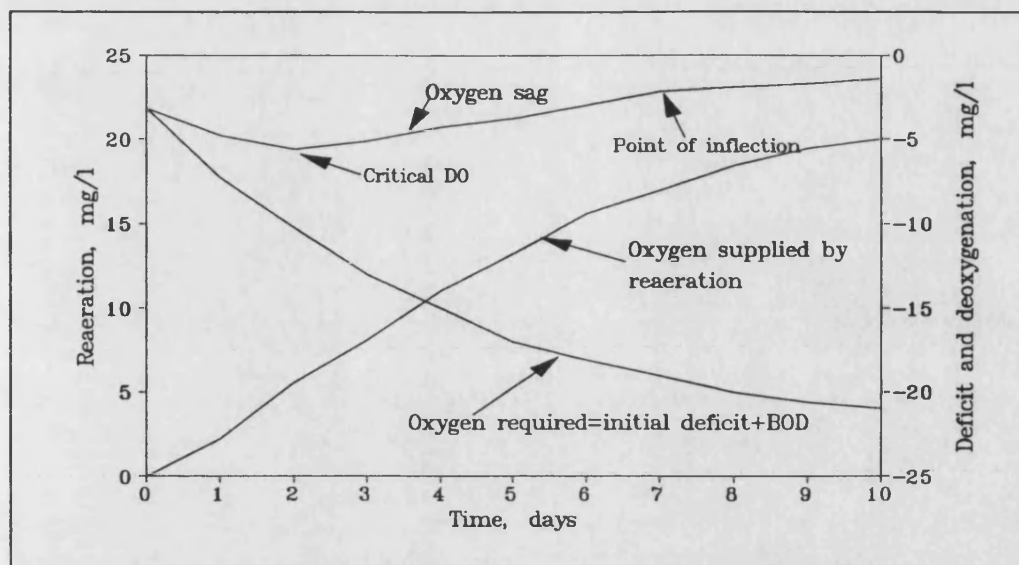


FIGURE 2.1: Typical dissolved oxygen sag for a polluted stream.

Discharged organic wastes are oxidized via two stages, (Shima *et al.*, 1976; and Courchain, 1962). First, organic material is oxidized by heterotrophs into $\text{NH}_4^+\text{-N}$, then this product is oxidized to $\text{NO}_2^-\text{-N}$ and to $\text{NO}_3^-\text{-N}$ successively by autotrophic bacteria (mainly *Nitrosomonas europaea* and *Nitrobacter winogradskyi* respectively). Thus if there is plenty of DO and organic material, and if the environment conditions are favourable, the growth of heterotrophs is very rapid and results in the decrease of both DO concentration and oxidizable organic material. Then the conditions become unfavourable for the growth and survival of heterotrophs. So that, DO concentration begins to increase again. Thus, there appears the first sag of DO profile. In spite of the recovering of DO concentration, heterotrophs would not grow again because of diminished oxidizable organic material and the accumulated $\text{NH}_4^+\text{-N}$, (Shima *et al.*, 1976).

Next begins the second stage of oxidation. The gradual growth of *Nitrosomonas europaea* and *Nitrobacter winogradskyi* causes the transformation of $\text{NH}_4^+\text{-N}$ into

NO_2^- -N and then to NO_3^- -N, so that DO concentration decreases again. Similarly, as in heterotrophs, the growth of autotrophs stops when oxidizable nitrogen is consumed, (Arceivala, 1981). Then they begin to decrease again rapidly, because of lowered growth rate and higher death rate. This leads to the other increase of DO concentration, which causes the second sag in DO profile, (Shima *et al.*, 1976). However, the DO deficit of the second sag is comparatively very deep.

The depth of the sag and the duration of low DO concentration due to nitrification are mainly dependent on the initial ammonium quantity or the discharged organic load and also on the growth rate of bacteria or growth limiting factors, (Shima *et al.*, 1976). The initial biomass of heterotrophs and the parameters which directly relate to heterotroph activity, do not have a large effect to the shape of the second sag. Equally, the parameters and the initial values related directly to the growth of nitrifying bacteria do not much affect the first sag in the DO profile, (Shima *et al.*, 1976).

The DO deficit reaches a maximum at the critical location. At that point, the uptake of oxygen due to BOD is balanced by the input of oxygen from the atmosphere and any algal or plant activity.

The decline in DO due to the nitrification process is a complex interaction between the various pathways that a given nitrogen form might take. This approach, therefore, requires estimates of the various coefficients and data on each of the nitrogen forms, (Thomann *et al.*, 1987).

As nitrifying bacteria are aerobic organisms, nitrification does not proceed under conditions of DO less than about 1 mg/l, (Thomann *et al.*, 1987). However, Arceivala (1981) stated that if the aeration capacity is not sufficient, nitrification will not occur even if other conditions are favourable and oxygen concentration should be 3 to 4 mg/l to avoid oxygen limitations. Nitrification can occur at lower levels, but the growth rate of nitrifiers is much slower. Eckenfelder (1989), indicated that DO level should be in excess of 2 mg/l for nitrification to occur. While in the case of the River Zarka it was found that a minimum of 3-4 mg/l oxygen is needed to promote the decay of ammonium, while more than 6 mg/l was needed for nitrate production, because of the high pollution status of the river.

The effect of salinity or chlorides is to reduce the saturation value. Thomann *etal.* (1987) reported the effect of salinity as incorporated by APHA (1985) as follows:

$$\ln C_{ss} = \ln C_{sf} - S \left((1.7674 \times 10^{-2}) - \left(\frac{1.0754 \times 10^1}{T} \right) + \left(\frac{2.1467 \times 10^3}{T^2} \right) \right) \frac{2.3}{4}$$

where:

C_{ss} = saline water DO saturation concentration (mg/l).

S = salinity in ppt, (1.80 * chlorinity in mg/l)

T = temperature in °K

C_{sf} = freshwater DO saturation concentration at 1 atm, (mg/l).

The River Zarka contains high amounts of dissolved salts as indicated by high values of chloride and electrical conductivity, thus its oxygen saturation value depends on salts as well as on temperature.

2.5.4- pH VALUE:

pH also has a considerable effect on nitrification rates and pH limits must range between 7.6 and 8.0 for maximum activity, (Arceivala, 1981; Shieh *et al.*, 1979; and Dodd *et al.*, 1974). Ammonia which is highly soluble, combines with hydrogen ions to form the ammonium ion, thus tending to raise the pH. In the neutral pH range, all of the ammonia is present in the ammonium form, and at a higher pH ammonia is evolved as a gas. The ammonia present in natural waters is thus a result of either the direct discharge of the material in wastewater or of the decomposition of organic matter in various forms, (Thomann *et al.*, 1987; and Joint Committee, 1977). An alkaline environment is required to neutralize acidic end products. Below a pH of 6.0, inhibition occurs, (Thomann *et al.*, 1987; and Prosser, 1990).

Optimum growth of nitrifying bacteria has generally been observed in the pH range of 8 to 9, (Joint Committee, 1977), although other ranges have been reported as 7.5-8.5, (Arceivala, 1981), and between 6 and 7.5, (Eckenfelder, 1989). Moore and Schroeder (1970) as cited by Arceivala (1981) found the range to be between 6.5 and 7.0. A substantial reduction in nitrification activity may be expected to occur at pH values below 7, although nitrification can occur at low pH.

The pH of the medium also has an appreciable effect on denitrification. Permissible pH ranges from 5.8 to 9.2, with the optimum between 7.0 and 8.2. At a pH above 7.0, nitrogen gas is reported to be formed almost exclusively, while below pH 7.0, intermediate forms of oxidized nitrogen escape from the medium, (Joint Committee, 1977).

Prakasam *et al.*, (1972) found that control of pH is unnecessary either in nitrification or denitrification of a concentrated nitrogenous waste, although the pH decreased as nitrification proceeded. They stated that adjusting the pH of nitrification between 5-11 did not increase the degree of nitrification, which indicated that there was no need to control pH in obtaining and sustaining nitrification in poultry wastewater.

Contradictory to the above, Sheih *et al.*, (1979) found that nitrification ceased at a pH of 6.5 with an optimum pH of 8.0. While, Wong-Chong *et al.*, (1978) found that the optimum nitrification rate was at a pH between 7.0 and 7.5. Furthermore, Dodd *et al.*, (1974) reported that pH had a marked effect on the efficiency of denitrification process, with increasing pH, nitrate yield decreased along with the growth rate. Ching-San *et al.* (1974) indicated that optimum nitrification efficiency occurs at a pH of 8.5 and a pH reduction to 7.0 and 6.5 will reduce the efficiency to 30% and 50% of the optimum. Harry *et al.* (1971) reported that pH did affect the rate of nitrification with an optimum pH of 8.4, as was also found by Wild *et al.*, (1971).

It seems that the dispute over the effect of pH and the optimum value for nitrification reported in literature could be attributed to methods of investigations and surrounding conditions. However, a mean value for pH in the Zarka over the study period ranged between 7.8 and 8.1. This range, as described by many authors is an optimum value for nitrification, and the small difference between minimum and maximum is insignificant for pH to be incorporated in a model.

2.5.5- ALGAE AND LIGHT:

Interference by algae with the treatment of water can be due to the changes they cause in pH, alkalinity, total hardness, and DO of the raw water, (Thomann, 1987), or to their increasing of the organic content carried by the water, (Palmer, 1980).

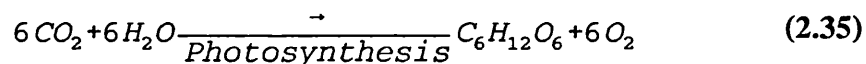
Algal growths have at least three important roles to play in gross freshwater nitrogen cycling (Starr *et al.*, 1981). First by assimilating nitrate, they reduce the nitrate concentrations *in situ*. Secondly, sedimentation of particulate algae is an important route whereby fixed nitrogen reaches the sediment, where it is rapidly mineralized. Thirdly, the primary producers provide the fixed carbon essential as an energy source for heterotrophic nitrogen organisms, especially, denitrifiers which hold the key to overall nitrate removal from freshwater.

Besides dissolved oxygen derived in nature from overlying atmosphere in streams and other water bodies, oxygen is released by green plants during photosynthesis. Although photosynthesis may make considerable amounts of oxygen available, oxygenation by green plants is confined to; (1) waters that are calm enough to encourage plant growth and (a) either not heavily polluted that green plants die off or (b) sufficiently recovered to reestablish the growth of green plants; (2) the hours of daylight; and (3) the warmer (growing) seasons of the year. During the night, aquatic plants abstract oxygen from the water and release carbon dioxide to it, (Fair *et al.*, 1971; and Sandoval *et al.*, 1985).

Although the incoming waters of the studied reach of River Zarka contains high

amounts of chlorophyll "a" as a measure of algal biomass, the algal activity is minimum and does not represent the high chlorophyll concentration due to the high pollutional status of the river, high light intensities and relatively fast waters (0.43 m/s). However, the Zarka catchment area has moderate sunshine hours and warm climate, but high light intensities.

The essence of photosynthetic process centres about these chlorophyll containing plants which can utilize radiant energy from the sun, convert water and carbon dioxide into glucose, and release oxygen. The photosynthesis reaction can be written as:



However, algae require oxygen for respiration, which can be considered to proceed continuously, while production of oxygen by photosynthesis occurs only during day light. Minimum values of DO usually occur in the early morning, predawn hours and maximum values occur in the early afternoon. In addition, aquatic plants require nutrients such as nitrogen and phosphorus for adequate growth as well as trace elements which are usually available in most water bodies, (Thomann, 1987). The Zarka waters contain high amounts of nitrogen and phosphate, thus nutrients are not growth limiting in the river. On the contrary, high amounts of ammonium (100 mg/l) is toxic to the aquatic life.

Light is important in streams, but it may be reduced due to high turbidity. Turbidities more than 30 ppm are high enough to cut off sunshine almost completely except for a shallow layer close to the surface. Turbidity usually seems to be the major limiting

factor in algal growth, (Palmer, 1980).

Sandoval *et al.* (1985) reported that incident solar radiation is an important environmental factor, which varies with time and position. Solar radiation is the energy source for the photosynthetic growth of algae. In a natural environment the light intensity to which algae are exposed to is not uniformly at the optimum value, but it varies as a function of depth due to turbidity (self-shading) and as a function of time of day. Thus algae in the lower layers are exposed to intensities below the optimum and those at the surface may be exposed to intensities above the optimum, so that their growth rate can be inhibited.

High light intensities of the Zarka ($479.2 \text{ cal/cm}^2 \cdot \text{day}$) could be over the optimum for algal growth because prolonged or sudden exposure to high light intensities leads to photodestruction of chlorophyll.

2.5.6- BIOCHEMICAL OXYGEN DEMAND, (BOD):

Biochemical oxygen demand (BOD), is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. The term "decomposable" may be interpreted as meaning that the organic matter can serve as food for the bacteria, and as energy, derived from its oxidation, (Sawyer *et al.*, 1978; and Shima *et al.*, 1978).

Effluent ammonia nitrogen poses an analytical problem in measuring BOD. At 20°C , nitrifying bacteria in raw domestic wastewater are usually insignificant in number and normally will not grow sufficiently during a 5-day BOD test to exert a measurable

oxygen demand. However, nitrifying bacteria very easily could be present in the treated effluent. To obtain a true measure of the treatment plant performance in removing organic matter, BOD tests may require correction for nitrification. The carbonaceous demand is usually exerted first, normally as a result of a lag in the growth of the nitrifying bacteria necessary for oxidation of the nitrogen forms, (Thomann, 1987). The correction involves inhibiting or correcting the nitrification in the BOD bottle, or measuring the ammonia to calculate the nitrogenous oxygen demand on the stream. Care must be taken when inhibiting nitrification to assure that no inhibition of the carbonaceous BOD occurs, (Joint Committee, 1977). The nitrogenous biochemical oxygen demand (NBOD) is often measured by adding a nitrification suppressant to the BOD bottle and therefore measuring only the carbonaceous BOD. If the BOD is also measured on an unsuppressed sample, NBOD can be obtained by the difference, (Thomann, 1987).

In shallow rivers a resident nitrifying population on the river bed may exert the majority of NBOD; planktonic nitrifiers are unimportant. This can readily be demonstrated by comparing the time course of nitrification within an isolated water sample with the nitrification which occurs during travel of water downstream.

It should be remembered, therefore, that 5-day BOD values represent only a portion of the total BOD. The exact percentage depends upon the character of the influent and the nature of the organic matter, and can be determined only by experiment. In the case of domestic and many industrial wastewaters, it has been found that the 5-day BOD value is about 70 to 80 percent of the total BOD. This is a large enough

percentage of the total so that 5-day values are used for many considerations. A 5-day incubation period was selected also to minimize interferences from oxidation of ammonia, (Shima *et al.*, 1978).

In the case of the River Zarka, the high content of nitrogen compounds in the river water forms a major part of BOD. This is more obvious at the sites where nitrification is minimum and nitrogen compounds are still un-nitrified.

2.5.7- CHEMICAL OXYGEN DEMAND (COD):

The chemical oxygen demand COD test is widely used as a means of measuring the pollutional strength of domestic and industrial wastes. This test allows measurements of a waste in terms of the total quantity of oxygen required for oxidation to carbon dioxide and water. As a result COD values are greater than BOD values and may be much greater when significant amounts of biologically resistant organic matter is present, (Sawyer *et al.*, 1978). The COD test has a higher precision than the BOD test. The standard deviation of the COD test has been found to be about 8% as compared to nearly 20% for the BOD test, (Arceivala, 1981).

As COD test measures the non-biodegradable as well as the ultimate biodegradable organics, change in the ratio of biodegradable to non-biodegradable organics affects the correlation between BOD and COD, (Joint Committee, 1977).

2.5.8- RIVER BED SEDIMENT:

Because of the lack of suitable techniques and practical difficulties, denitrification in marine sediments has long been left unexplored (Goering, 1978, and Muela *etal.*, 1988). Its importance has been increasingly understood in recent years. Although, the

significance of nitrification in marine sediments is largely unknown, (Carpenter *et al.*, 1983).

Comparison of potential nitrification activity PNA values and nitrifier counts in sediments and overlaying waters indicated that only 2% of nitrification in streams resulted from benthic organisms, (Prosser, 1990). Accumulation of benthic deposits in rivers can occur because of solids deposition during low-flow periods. In streams that receive secondary effluent, suspended solids (SS) that escape the treatment plant will contribute to these benthic deposits, (Kennedy *et al.*, 1986).

In the River Zarka, benthic oxygen demand cannot be substituted by oxygen produced by algal activity. An external oxygen source, like reaeration should be available to compensate for oxygen lost by benthic demand.

2.5.9- PROCESS INHIBITION:

The influence of temperature and substrate concentration on the rate of oxidation of nitrite by *Nitrobacter winogradskyi* has recently acquired some attention. Although, much contradictory information can be found in the literature, precise results may have been difficult to obtain.

The presence of toxic substances, even in small concentrations, can inhibit nitrifiers. Among these may be listed organic-sulphur compounds, phenols, cyanides (each capable of giving 75% inhibition at 10^{-5} to 10^{-6} moles), chromium, nickel, and zinc (at

about 0.25 mg/l each). Boron is known to be toxic to aquatic and plant life. High concentrations of boron in the River Zarka led in 1990 to an immense economical loss in Jordan in the areas depended solely on the river water for irrigation.

The observation that nitrification generally occurs after satisfaction of the carbonaceous demand has been explained by the toxic effect of carbon on nitrification, but is perhaps due more to the much slower growth rate of nitrifiers compared to the heterotrophs, (Arceivala, 1981).

There are several cases where produced material inhibits the process. Shima *et al.* (1978) and Prosser (1990) reported that it is possible that $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ are inhibitory to the growth of heterotrophs, *Nitrosomonas europaea* and *Nitrobacter winogradskyi* respectively.

Parkasam *et al.*, (1972) found that high ammonia concentration inhibited the growth of *Nitrobacter winogradskyi*, with the result of nitrite accumulation. The rate of nitrification decreased with an increase in the supplemented $\text{NH}_4\text{-N}$ concentration. Nevertheless, nitrification did not stop even at a 0.5M NH_4Cl concentration. In addition, Sheih *et al.*, (1979) reported that initial ammonium concentration was found to have a strong effect on the value of the kinetic parameters of the Michaelis-Menten rate expression at low ammonium levels. However, at high initial concentrations, both parameters attained a maximum value that was independent of the initial substrate level.

Wong-Chong *et al.*, (1978) observed that free ammonia inhibition was directly related to acclimatization where in some cases tolerance to concentrations as high as 50 mg N/l was observed, while in others, concentrations above 3.5 mg N/l were inhibitory. While Harry *et al.* (1971) found that nitrification is not inhibited at concentrations normally found in a domestic wastewater system as was also found by Wild, *et al.* (1971). Furthermore, Gee *et al.* (1990) also found that the substrate inhibition constant for ammonia is large (9,000 mg-N/l ammonia) which may be easily ignored in treating domestic wastewaters. But for the oxidation of nitrite they found that nitrite was inhibited by the concentration of nitrite only in the presence of a high concentration of ammonia and did not inhibit its own oxidation. They also found that the activity of *Nitrobacter winogradskyi* population was strongly dependent on the population of *Nitrosomonas europaea*, but not vice-versa. Nitrite oxidation in the absence of ammonia resulted in a very unstable system and required hydraulic-retention times of 10 days or greater to obtain complete nitrite oxidation.

Prosser (1990) cited the work of Keen and Prosser (1987), who found no evidence of substrate inhibition in continuous culture at the concentrations studied and also demonstrated limitations of the Monod equation in describing transient growth. However, the studied range was not mentioned when cited.

The study carried out by Wild *et al.* (1971) indicated that if nitrification system were run at 50 percent of the optimum conditions, the time required to oxidise the ammonia nitrogen completely would double or the volatile suspended solids (VSS) would have to be carried at twice the level necessary for complete nitrification under optimum

the river consists of rocks and stones and some muddy deposits during low flows.

Table (3.1) shows winter and summer depths, widths, velocities, and volumetric flow rates at all sites.

3.1.2- METHODOLOGY:

3.1.2.1- Sample collection:

Samples were collected from the ten sites on a monthly basis during the period from early May 1990 until late February 1992, representing all seasons. Another set of specific and comprehensive experiments were also carried out during 1993. The winter of 1990/1991 was characterized as an unusually dry season. The average rain-fall did not exceed 50% of the average annual rain-fall for the study area. Conversely, the winter of 1991/1992 was characterized as an unusually wet season. The average rain-fall exceeded 300% of the annual average. The sampling was stopped during this winter due to inaccessibility to the sampling sites. Samples were collected from points where stagnation and the effects of the stream edges and bottom are minimum to ensure complete mixing at the sampling point.

TABLE 3.1: Geometry of the different sites in summer and winter.

S I T E	SUMMER				WINTER			
	Depth (m)	Width (m)	Flow rate (m ³ /s)	Velocity (m/s)	Depth (m)	Width (m)	Flow rate (m ³ /s)	Velocity (m/s)
1	0.80	2.00	1.15	0.72	0.81	3.00	1.05	0.65
2	0.65	4.00	0.93	0.36	0.64	4.00	1.01	0.39
3	0.65	4.00	0.93	0.36	0.65	4.00	1.01	0.39
4	0.50	4.00	0.93	0.46	0.50	4.00	1.01	0.51
5	0.45	5.00	0.93	0.41	0.45	5.00	1.01	0.45
6	0.50	5.00	1.24	0.49	0.50	5.00	2.21	0.88
7	0.20	26.00	1.43	0.28	0.20	26.00	2.17	0.42
8	0.30	15.00	1.31	0.29	0.30	15.00	2.21	0.49
9	0.25	13.00	1.24	0.38	0.25	13.00	2.17	0.67
10	0.10	10.00	0.29	0.29	0.17	6.00	0.68	0.68

The monthly samples were used to measure seasonal variations of nitrogenous compounds as well as other water quality parameters, as described in the following sections. Dissolved oxygen, temperature, pH, EC and the redox potential were measured in the field.

3.1.2.2- Physical and chemical parameters:

3.1.2.2.1- Temperature and Dissolved Oxygen

The dissolved oxygen and temperature of the water samples were measured on site after calibrating the instrument according to the site altitude and the atmospheric pressure and temperature. A Yellow Springs Instrument (YSI), dissolved oxygen meter, model 58, was used to conduct these measurements. The accuracy of temperature measurement was $\pm 0.1^{\circ}\text{C}$ and for DO was $\pm 0.05 \text{ mg/l}$.

3.1.2.2.2- pH-Value

The pH value of the samples was measured on site using a WTW pH meter, model pH 91 which was calibrated prior to measurement using 4.00 and 9.00 buffer solutions with an accuracy of ± 0.1 .

3.1.2.2.3- Biochemical Oxygen Demand, BOD₅:

Upon return to the laboratory, the water samples were incubated at 20°C in a BSB-Controller, model 606T, WTW, for five days. Some times they were left for longer periods to monitor the second stage of the BOD curve, nitrogenous biochemical oxygen demand, NBOD. A known volume of water sample (depending on the amount of BOD expected) was incubated in an amber bottle fitted with a sodium hydroxide chamber. The sodium hydroxide will then react with CO₂ evolved due to carbonaceous oxidation. The resulting vacuum pressure will raise the mercury column attached to the bottle. The instrument was calibrated prior to each test. The accuracy of the instrument was $\pm 5\text{mg/l}$.

3.1.2.2.4- Nitrate, NO₃⁻

Nitrate was determined according to the standard methods for testing water and wastewater, (Greenberg *et al.*, 1980 and Abumoghli *et al.*, 1990). The samples were filtered through glass microfiber filters (Whatman), then 5-10 ml of the sample were taken, acidified with 2 ml of 1N HCl solution and the volume brought up to 100 ml. The absorbance was then read using a UV-spectrophotometer (Milton Roy, model spectronic 1201) at 206 nm with an accuracy of $\pm 0.1\text{ mg/l}$. Figure 3.2 shows the calibration curve for the nitrate test with a correlation coefficient of 0.97.

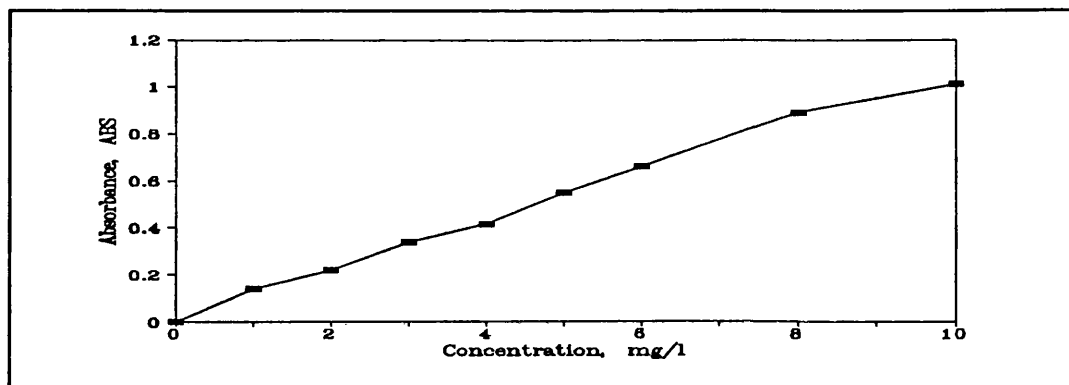


FIGURE 3.2: Nitrate determination calibration curve.

3.1.2.2.5- Nitrite, NO_2^-

Nitrite measurements were carried out according to Strickland and Parsons (1972). The water sample was filtered through GF/C glass microfiber filter. 50 ml, or aliquot brought to 50 ml with deionized distilled water, were treated by diazotizing with 1 ml of sulphanilamide and coupling with 1 ml of N-(1-naphthyl)-ethylene to form a highly coloured dye. The solution absorbance was then read at 543 nm with an accuracy of ± 0.05 mg/l using the above mentioned spectrophotometer. The calibration curve for nitrite determination can be seen in figure 3.3 with a correlation coefficient of 0.98.

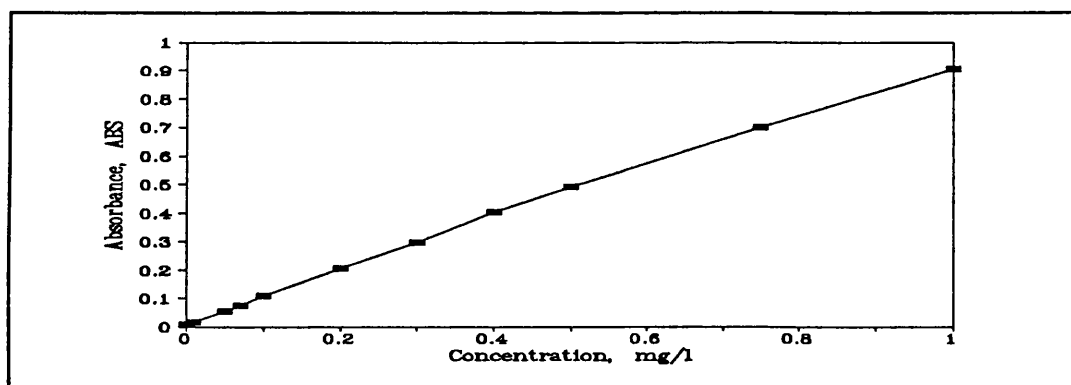


FIGURE 3.3: Nitrite determination calibration curve.

3.1.2.2.6- Ammonium ion Determination, NH_4^+ :

Ammonium ion determination was made according to Solorzano (1972) hypochlorite method. Water samples were treated in the field, and were kept in dark bottles, inside an icebox. After returning to the laboratory, standards were prepared and read along with the samples using the above mentioned spectrophotometer at a wavelength of 640 nm with an accuracy of ± 0.1 mg/l. Figure 3.4 shows the ammonium ion calibration curve with a correlation coefficient of 0.99.

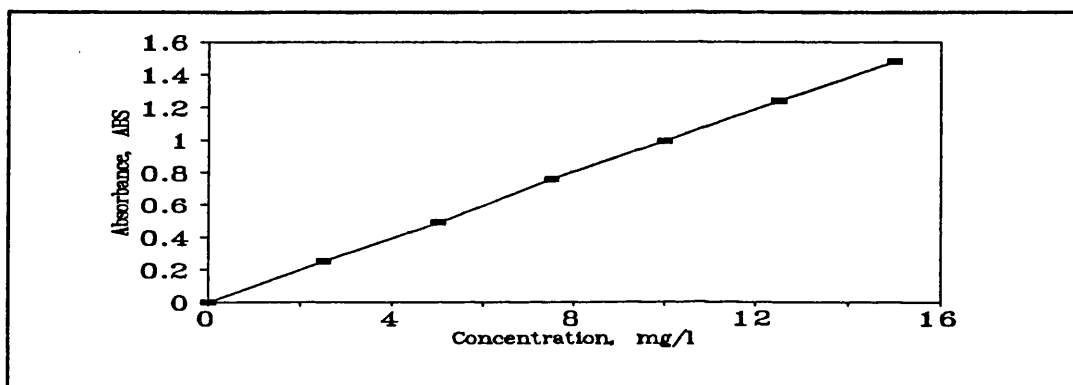


FIGURE 3.4: Ammonium ion determination calibration curve.

3.1.2.2.7- Total Organic Carbon, TOC; (Permanganate Value , PV):

PV determinations were made using standard methods for testing water and wastewater, (Greenberg *et al*, 1980 and Abumoghli *et al.*, 1990). The permanganate method was used by treating the sample with 33% NaOH and 0.01N KMnO_4 . The solution was then boiled for ten minutes, and titrated with 0.01N KMnO_4 after adding 25% H_2SO_4 and 0.01N oxalic acid. The accuracy of the method was ± 0.5 mg/l. The distilled water used for sample dilution was used as a blank and all results were corrected accordingly.

3.1.2.2.8- Chemical Oxygen Demand, COD:

The method described by the standard methods for testing water and wastewater, (Greenberg *et al.*, 1980 and Abumoghli *et al.*, 1990) was used for the determination

of COD. The sample was treated with potassium dichromate digestion solution and a silver sulphate catalyst, digested for 2 hours at 150°C and then titrated with ferrous ammonium sulphate solution with an accuracy of ± 0.5 mg/l. Two runs were carried out with deionised distilled water as a blank and all measurements were corrected accordingly.

3.1.2.2.9- Turbidity:

The turbidity of the sample was measured using a Hach spectro- photometer, model DREL/5, at a wavelength of 450 nm with an accuracy of ± 1 ftu. A filtered sample of distilled water was used as a blank with zero turbidity.

3.1.2.2.10- Salinity as Chloride:

Chloride was determined titrimetrically by titrating 10 ml of the sample with 0.01N silver nitrate (AgNO_3) solution using potassium chromate indicator with an accuracy of ± 0.2 mg/l.

3.1.2.2.11- Hydrogen Sulphide, H_2S :

Hydrogen sulphide was determined using Pachmayr's method (Abumoghli *et al.* 1990). The sample was treated with zinc acetate in the field to form zinc sulphide which is stable for several days. After returning to the laboratory, the sample was treated with dimethyl-p-phenylene diamine sulphate (DMPD) and with iron-III-ammonium sulphate. The solution was then brought to 100 ml with distilled water (free of sulphide) and measured using a spectrophotometer at a wavelength of 670 nm with an accuracy of ± 0.1 mg/l. The hydrogen sulphide content was calculated using the Beer-Lambert law. Distilled water free of sulphide was used as a blank.

3.1.2.3- BIOLOGICAL DETERMINATIONS:

3.1.2.3.1- Bacterial Count:

Bacterial samples were collected in sterile glass containers. The spread plate technique was used for the estimation of nitrifying and denitrifying bacterial counts. Serial dilutions of 1 ml were spread on agar plates of the relevant medium solidified with 1.5% agar. Plates of nitrifying bacteria were incubated at 28°C (being the optimum temperature for their growth, (Bergey's Manual, 1984) for 2 weeks. While the plates of denitrifying bacteria were incubated at 28 °C in an anaerobic container for one week. Three plates were incubated for each sample and for each dilution and the average was of the representative plates was taken.

The results were expressed as CFU/ml, (Colony Forming Unit per ml). The following media were used for this analysis:

3.1.2.3.1.1- Nitrifying Bacteria:

3.1.2.3.1.1. a- Ammonia Oxidizers:

The medium of Watson (1965) as described in Bergey's manual (1984) was prepared by dissolving the following in 1 litre of distilled water; $(\text{NH}_4)_2\text{SO}_4$ 1,320 mg, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 200 mg, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 20 mg, K_2HPO_4 114 mg, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.03 mg and 2 ml phenol red solution. The following trace elements were also added: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 1 µg, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 2 µg, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 2 µg, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 20 µg and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 100 µg.

After preparation of the medium, it was autoclaved for 15 min. at 121°C, adding, after cooling, the sterile phenol indicator. The pH was brought to 7.8-8.0 by adding sterile NaOH solution.

3.1.2.3.1.b- Nitrite Oxidizers:

The medium of Watson and Waterbury (1971) as described in Bergey's manual (1984) was used for nitrite oxidizer determinations. The medium was prepared by dissolving in 1 litre distilled water the following: NaNO_2 69 mg, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 100 mg, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 6 mg, K_2HPO_4 1.74 mg and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.03 mg. Also the trace elements listed in section 3.1.2.3.1.a were added. The medium was autoclaved at 121°C for 15 min. and the pH was brought to 7.8-8.0 by sterile NaOH solution.

3.1.2.3.1.2- Denitrifying Bacteria:

Alexander medium (1965) as described in Bergey's manual (1984) was used for enumeration of denitrifying bacteria. This medium was prepared by mixing two different solutions: Solution 1 was prepared by dissolving 1 g of KNO_3 , 1 g of Asparagine and 5 ml of bromothymol blue indicator in 500 ml distilled water. Solution 2 was prepared by dissolving in 500 ml distilled water, sodium citrate 8.5 g, KH_2PO_4 1 g, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 1 g, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 0.2 g and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.05 g. The two solutions were mixed after being autoclaved at 121°C for 15 min. and the pH was brought to around 7.0 by adding sterile NaOH solution.

3.1.2.3.2- Chlorophyll "a":

A known volume of a water sample was filtered through GF/C glass-fibre filter. The filter was then preserved in 10 ml 90% acetone solution and kept overnight at 4°C in the dark. The sample was then extracted by centrifuging for 20 min. at 3000 rpm, then transferred to a 1 cm cuvette of a spectrophotometer. The optical density was read at 630, 645, 663, and 750 nm. The following equation was used to calculate chlorophyll "a" in $\mu\text{g/l}$, (Greenberg *et al.*, 1980; Holm-Hansen 1978; and Abumoghli *et al.*, 1990):

$$C_a = [((11.64 (O_{d663}) - 2.16 (O_{d645}) + 0.1 (O_{d630})) \pm (O_{d750}))] / V \quad (3.1)$$

where:

C_a is Chlorophyll "a" ($\mu\text{g/l}$),

V is the volume of the filtered sample (l), and

$O_d(n)$ is the optical density at n wavelength.

The accuracy of test was $\pm 10\mu\text{g/l}$.

3.1.2.4- Sediment content analysis:

3.1.2.4.1- Nitrogenous compounds:

Nitrate and ammonium nitrogen concentrations of the fresh sediment were determined as follows:

Extracts were prepared by shaking 10 g of sediment in either 50 ml of deionized water, for nitrate, or 50 ml cation eluent (7 mM HCl), for ammonium nitrogen, for 1hr, and filtering through Whatman No. 40, (Wyer and Kay, 1989). The extracts were measured as mentioned in sections 3.1.2.2.4 - 6.

3.1.2.4.2- Bacterial content:

One gram of a sediment sample was taken aseptically and added to 9 ml of Ringer's solution. The mixture was shaken and serial dilutions of 1 ml were taken and spread on agar plates of relevant medium for determination of different bacterial types mentioned in section 3.1.2.3.

3.2- BATCH EXPERIMENTS:

Batch experiments were carried out to simulate the river system in the laboratory, where a batch experiment can represent a reach of the river which is assumed to be a well mixed reactor.

3.2.1- River Zarka water and activated sludge effluent:

A set of sampling runs were carried out to find rates (ammonium decay and nitrate production rates), constants and coefficients (of the model to be developed representing the different parameters involved, i.e. BOD decay coefficient, ammonium decay rate coefficient, etc.) of the relative processes. These runs were carried out in a batch mode in the laboratory during two periods; the first was during the spring and summer of 1991, and the second one was carried out during the spring of 1993 which was modified to include latest work. The activated sludge experiments were carried out on wastewater collected from a Wessex Water plc. wastewater treatment plant located at Avonmouth, England.

Samples from the different sites along the Zarka were shipped in an ice-box within 3-4 hours of collection. These batch experiments included the following (described in details in chapter 5) noting that all samples were measured under forced aeration and incubated at 25°C (optimum for bacterial growth), unless otherwise stated:

- 1- One field visit was dedicated to find out whether the samples Shipped in a battery operated fridge (to be measured in the laboratory) within 3-4 hrs of collection exhibits different behaviour than those collected and directly measured on site, or they give the same rates of change. It was found that both sets of samples give the same results after eliminating the effect of temperature change over the period of the field test.
- 2- To measure the algal contribution on the nitrification process, two sets of samples were collected; the first one was subjected to light and the second was

covered with a black hood, as soon as collected from the river. This will give an estimation of the photosynthetic activity in the process.

- 3- River bed sediment exerts an extra oxygen demand on the water. Therefore to measure the amount of this contribution, a set of samples were collected and to the bottom of the container a measured amount of sediment was added. The height of the water column above the sediment was chosen to represent the actual depth of the river. This experiment was repeated by covering the samples with a black hood to measure the photosynthetic activity in the presence of sediment. This experiment was repeated by adding the sediment to a sterile river water column. This will represent the sediment demand alone.
- 4- Another two sets of samples were taken and filtered through two different types of filters, Whatman no. 40 to remove suspended matter keeping the microorganisms, and 0.3 μm filters to remove microorganisms from the water. This experiment will indicate the contribution of suspended solids as algae and the contribution of microorganisms to the system, respectively.
- 5- The dissolved oxygen consumption rate was followed on-site by submerging a sample bottle in the river to keep the same surrounding conditions of the river, then the dissolved oxygen was measured over 30-60 min. Again, this was repeated at each site by immediately covering the sample to prevent light penetration. This experiment will give an indication of the photosynthetic activity and oxygen consumption rate under true conditions.
- 6- Again the sediment oxygen demand was measured by adding river bed sediment to the columns.

- 7- The diurnal variation of oxygen and temperature was followed by measuring the dissolved oxygen of the different sites over 24 hours by taking hourly samples.
- 8- The minimum concentration of dissolved oxygen necessary to promote nitrification was measured by applying different aeration rates to the incubated samples.
- 9- Temperature affects all reactions especially those involving microorganisms. Therefore, to measure the temperature effect on the nitrification process of River Zarka, samples from the different sites were incubated at different temperatures, 15, 20 and 25°C (mean temperatures of River Zarka during different seasons).
- 10- Cell concentration is not the same all over the year, and also it is affected by the degree of treatment at the wastewater treatment plant. Therefore, samples were collected and diluted by filtered river water (bacteria free river water) to different cell concentration levels and nitrogenous compounds were measured over the following 5-6 hrs.
- 11- To measure the change in the nitrogenous compounds of a parcel of water travelling along the river, the time of travel needed by this parcel to move from one site to another was measured and sampling was scheduled accordingly.
- 12- Settling or resuspension rate was measured by measuring the total suspended solids at the different sites along the river course.
- 13- The nitrogen content as well as the bacterial content of the river bed sediment was measured to monitor the interaction between river water and the sediment.

- 14- Chlorophyll "a" concentration at each site was measured and related to the dry weight of algae.

3.2.2- Pure culture experiments:

Pure cultures of *Nitrosomonas europaea* (NCIMB 11850), *Nitrobacter winogradskyi* (NCIMB 11846), *Pseudomonas fluorescens* (Bath University culture) and *Alcaligenes xylosoxidans subsp. xylosoxidans* (NCIMB 11015), all ACDP group 1, were incubated in the relevant liquid medium (as described below) for different incubation periods and at different laboratory conditions as in the previous section. All conditions used for testing the river water and the activated sludge effluent were used in the testing of the pure cultures, as long as the conditions were applicable.

For pure culture experiments, a 2 or 5 litre fermenters were prepared as in figure (3.5), which illustrates the following connections:

- An inlet tube connected to an air (or nitrogen) supply provided with a heppa vent air filter. Gas was used to provide the fermenter with oxygen (or nitrogen) and mixing. The tube extended to the bottom of the fermenter to ensure complete mixing. Oxygen concentration was kept constant during these experiments by continuously measuring DO in the medium and the flow rate of air was accordingly regulated, i.e. when a drop in DO was observed, the air flow was increased to restore initial DO concentration.
- An outlet tube for exhaust gas, also provided with an air filter.
- A sampling tube connected to a perstatic pump for sampling. The end of the tube was connected to a stainless steel tube fitted with a valve. The stainless steel tip was flamed before each sampling to prevent contamination. The

pumping time was preset to pump an initial amount to flush any remains in the tube, then to give the required volume of sample.

- A water bath to provide the required incubation temperature connected to a chiller for lower temperatures.
- The fermenter was filled with the required media and autoclaved with all connections at 120°C for 15 min. It was then left to reach room temperature before cell incubation.
- The pH of the media was monitored through out the experiment and was regulated by adding a sterile alkaline solution if it fell below 7.8-8.0.

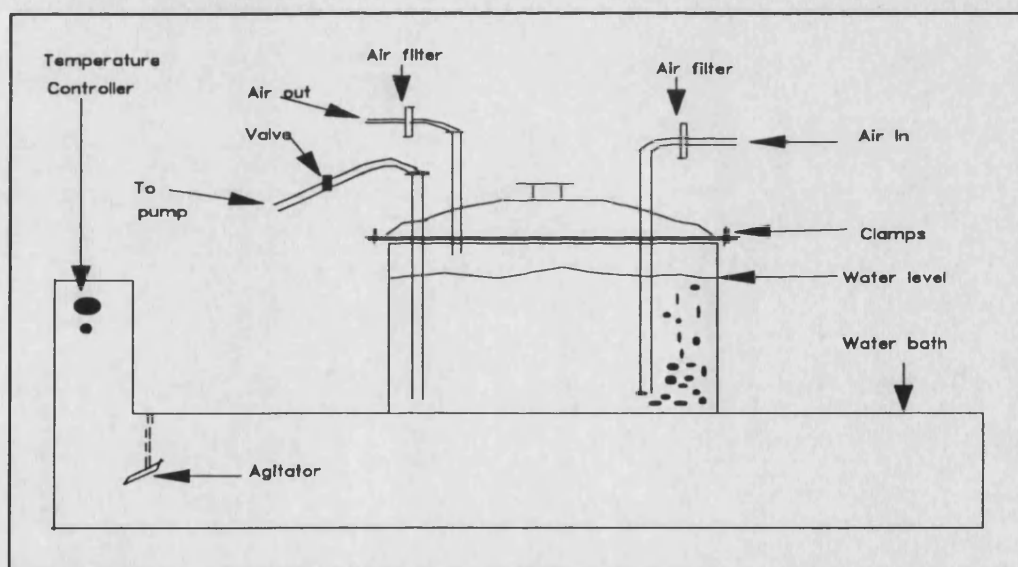


FIGURE 3.5: Layout of fermenters used in laboratory batch experiments.

In the case of denitrifying bacteria in the pure culture experiments, anaerobic conditions were kept by stripping out the oxygen by nitrogen gas and providing the fermenters with oxygen traps to prevent oxygen from entering into the system when sampling. Mixing in this case was provided by incubating the fermenters in a shaker incubator at the relevant temperature.

3.2.2.1- Media of denitrifying bacteria:

The medium described in this section and in the following sections are almost the same as the previously mentioned medium (section 3.1.2.3). The only difference is that it was found that some materials and the formed colours in the previous medium causes an interference in the optical density when measuring nitrate, nitrite and ammonium. Therefore, other compounds were used to eliminate any possible interference.

Minimal Medium for isolating and incubating denitrifying bacteria, *Pseudomonas* and *Alcaligenes*, (Mortimer *et al.* 1981, and Bergey's manual 1984):

The following recipe gives 1 litre liquid medium. The medium is prepared and autoclaved as three separate solutions.

Solution A:

K ₂ HPO ₄ ·3H ₂ O	0.87	g
KH ₂ PO ₄	0.54	g
KNO ₃	5	g
(NH ₄) ₂ SO ₄	1	g
Carbon source	4	g
Distilled water	980	ml

Solution B

(magnesium sulphate stock solution):

MgSO ₄ ·7H ₂ O	2	g
Distilled H ₂ O	100	ml

Solution C (trace salts stock solution):

CaCl ₂ ·2H ₂ O	0.2	g
FeSO ₄ ·7H ₂ O	0.1	g
MnSO ₄ ·H ₂ O	0.05	g
Na ₂ MoO ₄ ·2H ₂ O	0.01	g
CuSO ₄ ·5H ₂ O	0.01	g
0.1 N HCl	100	ml

10 ml of solution B and 10 ml of solution C were added to solution A aseptically.

Another liquid medium (below) was used for the incubation of denitrifying bacteria as described in the catalogue of strains (1990). This medium was used as a maintenance medium for denitrifying bacteria which was kept at 5°C. Also, another set of experiments were carried out using this medium to find out any possible differences between the two different types of medium.

Nutrient broth (OXOID CM3) which contained:

Lab-lemco beef extract	1.0 g
Yeast extract	2.0 g
Peptone	5.0 g
NaCl	5.0 g
Distilled water	1.0 litre

The medium was autoclaved at 121°C for 15 min. When a solid medium was needed, 15 g/l agar was added before autoclaving.

3.2.2.2- Media for nitrifying bacteria:

Nitrosomonas europaea and *Nitrobacter winogradskyi* were incubated and maintained in the following media as follows:

Medium for ammonia-oxidizing bacteria, *Nitrosomonas europaea*, (Dando and Young, 1990).

KH ₂ PO ₄	200 mg/l
(NH ₄) ₂ SO ₄	235 mg/l
MgSO ₄ .7H ₂ O	40 mg/l
CaCl ₂ .2H ₂ O	40 mg/l
FeSO ₄ .7H ₂ O*	0.5 mg/l
NaEDTA*	0.5 mg/l
Phenol red*	1.0 mg/l
Distilled water	1.0 litre

* these are prepared as separate stock solution as follows:

FeSO ₄ .7H ₂ O	90.0 mg
NaEDTA	50.0 mg
Phenol red	50.0 mg
Distilled water	200 ml

Two millilitres of the stock solution were added per litre of medium. The medium was autoclaved at 121°C for 15 min. After autoclaving, sterile 5%Na₂CO₃ was added until the medium turned pale pink. Further Na₂CO₃ was added during incubation to restore pink coloration. When no further colour change occurred, growth was complete. The bacteria were grown in the dark. When solid media was needed, 15 g/l of agar was added before autoclaving.

Medium for Nitrite-oxidizing bacteria, *Nitrobacter winogradskyi*:

The same medium described above was used except that (NH₄)₂SO₄ was replaced by NaNO₂ (247.0 mg/l).

Liquid stock cultures of nitrifying bacteria were stored in the dark at 15°C and transferred every 4-6 months. Ammonia oxidizing bacteria were maintained in a medium containing 25 mg of NH₃-N/l, 0.001% phenol red, 0.5 M HEPES buffer at pH 7.8-8.0, and appropriate salts (as above). When the colour changed from red to yellow (indicating that most of the ammonia has been oxidized) additional ammonia was added and the pH adjusted with 1M K₂CO₃. Stock cultures of nitrite-oxidizing bacteria were maintained in an appropriate medium as above.

CHAPTER FOUR

WATER QUALITY OF RIVER ZARKA

4.1- INTRODUCTION:

The main continuous source of the river is the waste stabilization pond's (WSP) effluent. WSP have been proved to be qualitatively and quantitatively overloaded. The river receives high amounts of phosphate (44.6 mg/l PO_4) as a result of the type of detergents used in houses. These detergents also contain considerable amounts of boron which also originates from the industries located upstream of the river. Boron is a toxic substance to aquatic life as well as to vegetation. In 1990 the country experienced a major economical loss when the river water was used for irrigation without mixing the water with other fresh water resources. The main reason was found to be the high boron concentrations in the river water.

Furthermore, the Ruseifeh town which discharges its wastes into the Zarka system either by direct connection to the sewer network, which eventually reach the river, or by floods which carry all deposited phosphate minerals from that area which is well known of its phosphate mines.

The wastewater from the three cities connected to the same sewer network (Amman, Ruseifeh and Zarka with a total population of 2.2 million) reach the river after passing through the waste stabilization lagoons. The wastewater is carried by a 39 km long closed pipeline before discharging into the lagoons. The anaerobic environment created within the pipeline exerts high oxygen demand, therefore creating a suitable

environment for hydrogen sulphide to be formed (3.0 mg/l in the influent). Also associated with the anaerobic environment, acidic medium is highly feasible leading to lower pH values (below 6.9), high redox potential (-1.7 mV) and high chemical oxygen demand COD (1100 mg/l).

After passing the maturation ponds, the wastewater is chlorinated in a final and separate pond. Chlorine is injected into the pond and the water flows in a zigzag route to increase the contact time. However, chlorination is infrequent and depends on the availability of chlorine. The infrequency in chlorination will add a difficulty in modelling the effect of chlorination on cell concentration and algal biomass as well as on the different nitrogen compounds which can react with chloride to form chloramines.

All the above mentioned problems explain the inadequacy of the treatment within the lagoons which eventually produce a bad quality effluent affecting therefore the quality of the river water. However, the BOD reduction in the WSP is around 90% efficient, but the effluent still contain high amounts of other pollutants.

Collection of monthly water samples started early May 1990 until February 1993 for the determination of water quality parameters. Measurements were carried out over two periods for the determination of model constants and coefficients (as mentioned in section 3.2). The first period was during 1991 and the second during 1993.

The analyses were carried out for all sites. The wastewater treatment plant influent and

the Sukhneh stream (the sole tributary of River Zarka) water quality were also studied.

The analyses included:

- Nitrate NO_3^- ,
- Ammonium ion NH_4^+ ,
- Nitrite NO_2^- ,
- Phosphate PO_4^{3-} ,
- Chloride Cl^- ,
- Total Organic Carbon TOC,
- Chemical Oxygen Demand COD,
- Biochemical Oxygen Demand BOD,
- Chlorophyll "a",
- Microorganisms (total count, faecal and total coliform, nitrifiers, and denitrifiers),
- Turbidity, pH, temperature, DO and Eh were measured on site.

Description of the water quality of the Zarka helps in understanding the quality problems, and allows for the determination of model parameters. Table (4.1) shows average values of all tested parameters along the river over the study period.

TABLE 4.1: Measured quality parameters at all sampling sites along the river

PARAMETER	St. Error of test	Site 2			Site 3			Site 4			Site 5			Site 6			Site 7			Site 8			Site 9		
		AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX
Depth (m)	± 0.01	0.65	0.6	0.7	0.75	0.70	0.80	0.5	0.45	0.55	0.45	0.4	0.5	0.5	0.45	0.55	0.22	0.18	0.25	0.29	0.25	0.32	0.25	0.21	0.28
Distance (km)	± 0.10	0.00	0.0	0.0	3.00	3.0	3.0	7	7	7	15	15	15	17	17	17	22	22	22	37	37	37	42	42	42
pH value	± 0.2	7.93	7.5	8.3	8.0	7.52	8.4	8.2	7.8	8.6	8.0	7.6	8.3	7.7	6.85	8.52	7.8	7.0	8.5	7.9	7.2	8.5	7.8	7.3	8.3
Temperature°C	± 0.1	16.3	6.7	25.9	16.4	6.7	26.0	17.8	8.4	27.2	17.7	7.5	27.8	18	6.6	29.3	17.7	6.5	28.9	17.5	6.2	28.7	17.6	6.1	29.1
DO (mg/l)	± 0.05	4.1	2.0	6.2	7.0	4.0	9.9	5.5	2.1	8.9	4.05	2.1	6.0	5.7	2.6	8.8	6.4	3.9	8.8	6.7	4.5	8.9	6.6	3.7	9.5
PO4 (mg/l)	± 0.1	47.5	26.0	69.0	41.2	13.1	69.3	39.6	15.9	63.2	30.2	5.9	54.4	31.2	9.2	53.2	24.5	9.0	40	22.0	9.7	34.2	17.9	8.7	27
Cl (mg/l)	± 5	406	319	492	351	277.9	424.2	351	277.9	424	387	305	468	400	333	468	408	333	484	372	295	448	403	330	476
TOC (mg/l)	± 5	228	124	331	205	100	309	168	92.3	243	193	121	266	146	34.5	257	116	44	189	64.9	24	145	79.5	19	140
COD (mg/l)	± 3	347	206	487	269	190	348	263	194	331	226	145	307	203	74.2	331	144	57	231	104	57	150	99.5	48	151
BOD (mg/l)	± 0.5	81	32.5	130	67.5	25	110	63	25	100	53.5	19.5	87.4	48	15	80.1	34.3	5.0	63.6	28.5	5.0	52	23	2.0	44
Turbidity (ftu)	± 0.2	165	20	310	150	60	240	191	62	320	373	58	315	139	0.0	278	142	25	258	71	22	120	46.5	15	78
Chlorophyll "a" (µg/l)	± 10	430	210	650	557	200	914	533	58	1009	386	173	600	324	19.8	630	257	145	370	153	38	267	160	40	281
Nitrobacter*	± 0.1	30	10	50	100	50	150	70	50	50	70	100	85	115	60	55	65	20	28	32	18	24	6	5	7
Nitrosomonas *	± 0.1	40	20	60	80	60	100	100	60	100	60	100	80	120	50	48	52	30	28	32	18	24	5	3	7
Denitrifiers *	± 0.1	50	20	80	90	70	110	100	60	100	60	100	90	110	70	75	65	30	28	32	8	12	3	2	4
HS (mg/l)	± 0.05	0.3	0.2	0.4	0.3	0.2	0.4	0.2	0.0	0.4	0.25	0.1	0.4	0.15	0.0	0.3	0.1	0.0	0.2	0.1	0.0	0.05	0.05	0.0	0.1
Total count *	± 0.1	30	10	50	200	100	300	70	55	70	200	180	220	80	90	70	80	30	28	32	8	12	4	3	5
NO3-N (mg/l)	± 0.1	7.1	3.6	10.6	5.6	2.1	9.0	8.6	3.2	14.0	15.6	2.5	14.1	9.4	3.4	15.4	11.9	6.0	17.8	16.9	7.3	26.5	18.5	7.0	30.0
NO2-N (mg/l)	± 0.05	0.2	0.0	0.4	1.4	0.0	2.7	1.8	0.0	3.6	4.7	0.0	9.4	4.9	0.1	9.7	4.2	0.1	8.3	3.5	0.3	6.6	3.3	0.1	6.4
NH4-N (mg/l)	± 0.1	85.6	61.2	110	82.9	60.2	105.6	78.1	52.2	104	173	57.4	116	66.1	46.3	85.9	49	29.4	68.9	27.5	10	45	23.4	2.8	44
Flow rate,m ³ /s	± 0.05	1.05	0.9	1.2	1.05	0.9	1.2	0.37	0.9	1.2	1.05	0.9	1.2	2.5	0.9	4.1	2.5	0.9	4.1	2.5	0.9	4.1	2.5	0.9	4.1
Velocity (m/s)	± 0.01	0.4	0.3	0.5	0.39	0.33	0.45	0.5	0.4	0.6	0.45	0.4	0.5	1.0	0.36	1.65	0.5	0.2	0.8	0.55	0.2	0.9	0.8	0.3	1.3

*x10⁵(cfu/ml)

Figure 4.11: However, the seasonal and diurnal temperature variation affects rate of nitrification. This fact was investigated by incubating the river water at different temperatures, 15-25°C, (section 5.4.1). This experiment showed that nitrification increases with temperature. Hence, the effect of temperature should be included in modelling the decay term as a correction factor for nitrification rates and coefficients. μ_{nitr} can be written as follows, $\mu_{nitr} = \mu_{nitr,20} \cdot \theta^{T-20}$, where $\mu_{nitr,20}$ is the nitrification rate constant at 20°C, θ is the temperature correction coefficient, and T is the temperature in °C.

4.2- RIVER WATER (SITE 2 TO SITE 9):

4.2.1- pH- VALUE:

The pH value, is an important factor affecting nitrification and denitrification processes, as a consequence of its effect on the microorganisms and on the oxidation of nitrogen compounds.

Many authors have reported different ranges of optimum pH, (Billen, 1975; Joint Committee, 1977 and Arcievala, 1981). They all agreed that nitrification and denitrification activities are reduced below pH 7.0. The pH of the Zarka is slightly alkaline with a minimum value of 7.88 measured at site 6 and a maximum of 8.07 measured at site 4 (figure 4.1). The small difference between minimum and maximum is not considered significant enough to be incorporated in the model, but indicates that the pH of the river favours nitrification.

4.2.2- TEMPERATURE:

The optimum temperature for river purification is considered to be between 25-35°C, (Eckenfelder, 1989). Therefore, having a mean temperature of 19.3°C at site 3 and 21.7°C at site 9 throughout the study period indicates a favourable temperature for nitrification, (figure 4.1). However, the seasonal and diurnal temperature variation affects rate of nitrification. This fact was investigated by incubating the river water at different temperatures, 15-25°C, (section 5.4.1). This experiment showed that nitrification increases with temperature. Hence, the effect of temperature should be included in modelling the river water as a correction factor for nitrification rates and coefficients.

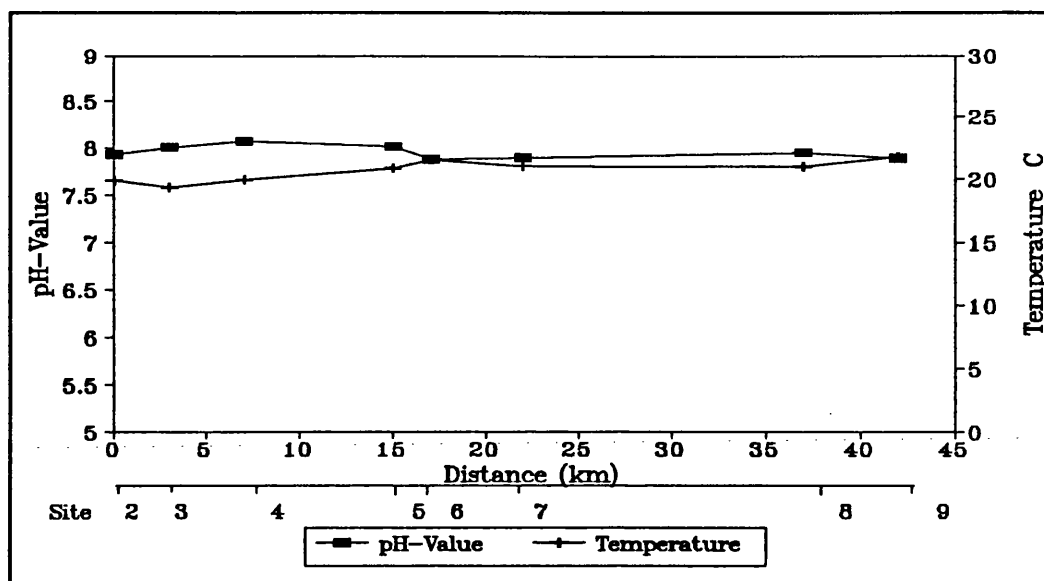


FIGURE 4.1: Temperature and pH variation along the river.

In summer time, with an average temperature of 26.2°C, the conditions are ideal for nitrification. This explains high nitrate, nitrite and ammonia concentrations in summer and in the batch experiments at 25°C. In winter the temperature drops down to a minimum of 10°C, at which conditions are not ideal for nitrification. Although, several investigators have reported nitrification to occur at temperatures as low as 5°C, (Eckenfelder, 1989).

The increase in temperature along the river is attributed to time of sampling (9-10 am at site 2 and 11-12 am at site 9). However, diurnal temperature variation measurements show that there is a wide range (around 10°C) in temperature over 24 hrs (section 5.4.6), which is a characteristic of a shallow river that highly responds to the environmental changes.

4.2.3- DISSOLVED OXYGEN:

As nitrifying bacteria are aerobic organisms, nitrification does not proceed under conditions of DO less than about 1 mg/l, (Thomann *et al.*, 1987). However, Arceivala

(1981) stated that if the aeration capacity is not sufficient, nitrification will not occur even if other conditions are favourable and oxygen concentration should be 3 to 4 mg/l to avoid oxygen limitations.

The DO curve, (figure 4.2) illustrates a clear DO sag at site 4. The increase in DO levels after site 5 indicates that mixing of the two streams (the River Zarka with low DO content and Al-Sukhneh tributary with high DO content) does not add significant oxygen due to the low flows of the tributary. The first increase in DO concentration is attributed to the original low content, of the outfall, of microorganisms which allows oxygen to build up. Thereafter, a decrease in DO is noticed after heterotrophs have utilized the available oxygen for their growth and for ammonia oxidation into nitrite and nitrate.

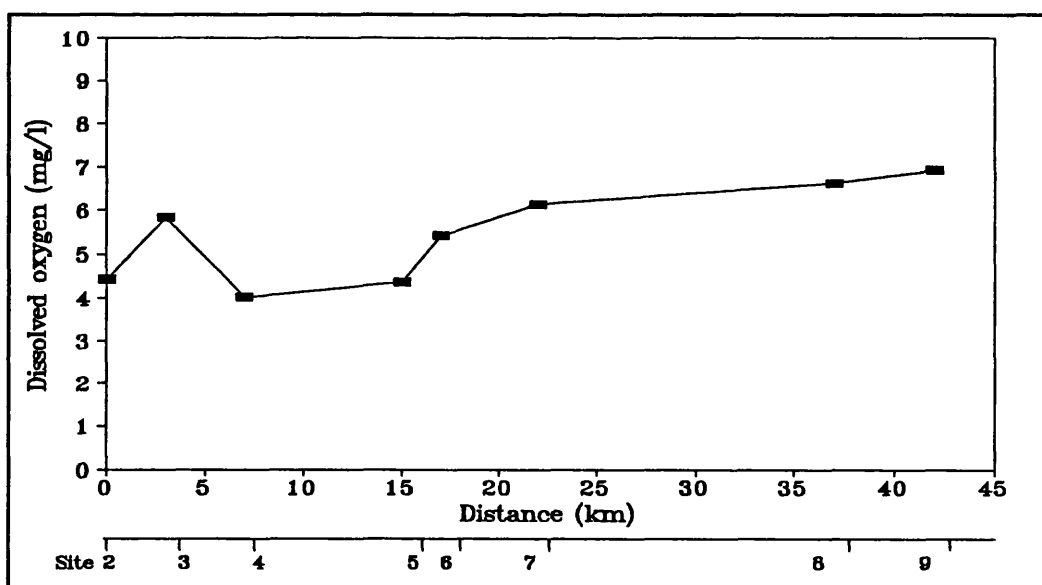


FIGURE 4.2: Dissolved oxygen variation along the river.

Generally, the second sag occurs when the growth rate is slower than the death rate, which causes an increase in DO concentration. The continuous increase in DO levels in River Zarka water suggests that oxygen entering the system is higher than that

utilized by the different oxygen sinks.

Nitrification can occur at lower oxygen levels, but the growth rate of nitrifiers is much slower at these levels. Eckenfelder (1989), indicated that DO level should be in excess of 2 mg/l for nitrification to occur. While Arceivala (1981) reported a value between 3-4 mg/l. This was investigated by performing a set of experiments for nitrogen transformation at different oxygen concentrations, (section 5.4.5). This section shows that increasing oxygen concentrations increases rates of nitrification. The minimum oxygen level needed to enhance nitrification in River Zarka was found to be between 3-4 mg/l for ammonium decay and more than 6 for nitrate production.

4.2.4- NITRATE NO_3^- , NITRITE NO_2^- , AND AMMONIA AS NH_4^+ :

The river water contains high amounts of ammonium, (figure 4.3) with a maximum at site 2 (the wastewater plant effluent) and decrease slowly until site 5 (at km 15), after which the decrease is at a much higher rate. As a consequence, nitrate increases slowly until site 5 then the rate of increase is much higher. Nitrite has an unstable nature, and as an indication of nitrification, it tends to build up and then decreases again. The river, after site 5, takes a wider route and becomes shallower, hence increases turbulence, and in turn increases aeration and consequently nitrification.

Deoxygenation of river dissolved oxygen was also followed on site, (figure 4.4) which shows that, as a consequence of higher rates of nitrification after site 5, and the increase in river reaeration, the overall deoxygenation rate is lower at downstream sites than at upstream sites where oxygen demand is higher as also indicated by BOD_5 values. This will be discussed in more details in chapter five.

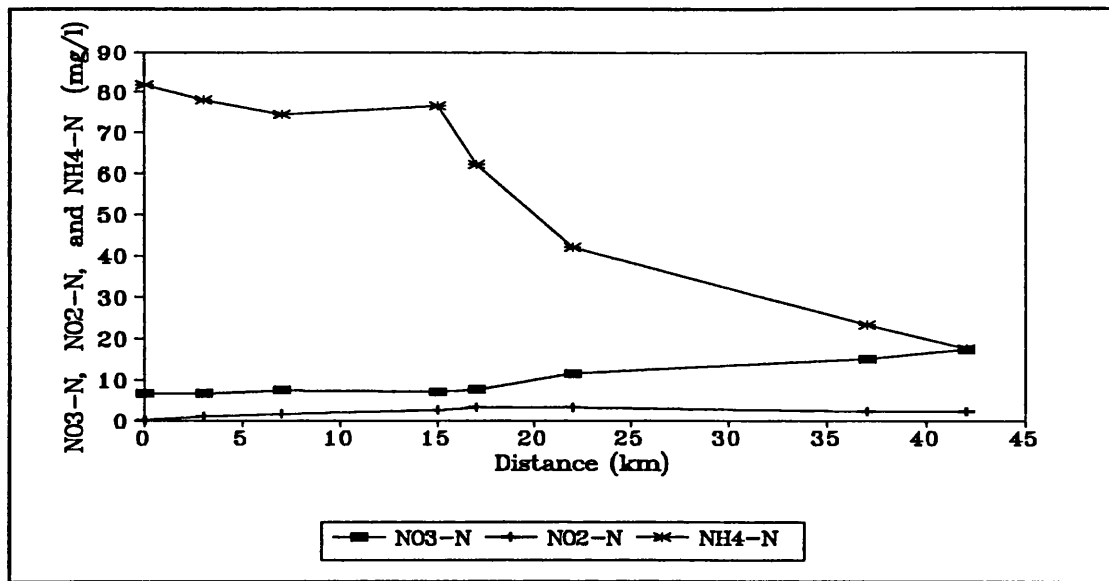


FIGURE 4.3: Nitrate, nitrite and ammonium concentration variation along the river.

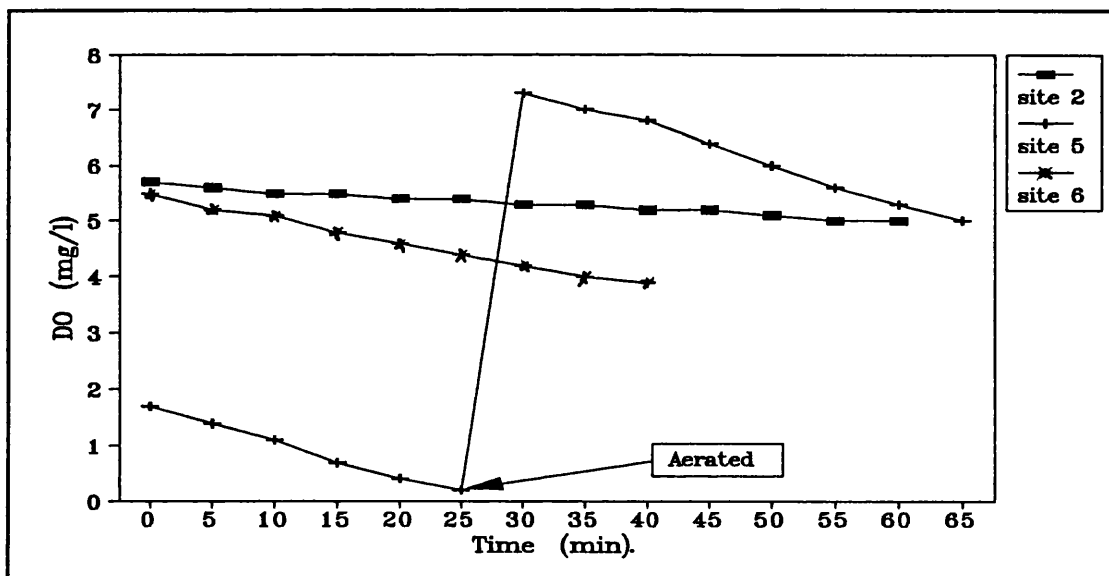


FIGURE 4.4: On-site deoxygenation rate at sites 2, 5, and 6.

4.2.5. PHOSPHATE, PO_4^{3-}

Phosphate concentrations were measured as orthophosphate PO_4^{3-} . Figure (4.5) shows the decrease in phosphate levels along the river as a consequence of self purification.

The high content of phosphate provides aquatic life in the river with sufficient amounts of nutrients. Thus, phosphate is not growth limiting, (Salameh *et al.*, 1987).

The high content of phosphate is believed to be as a result of using detergents of high

phosphate content as well as from phosphate mines located nearby.

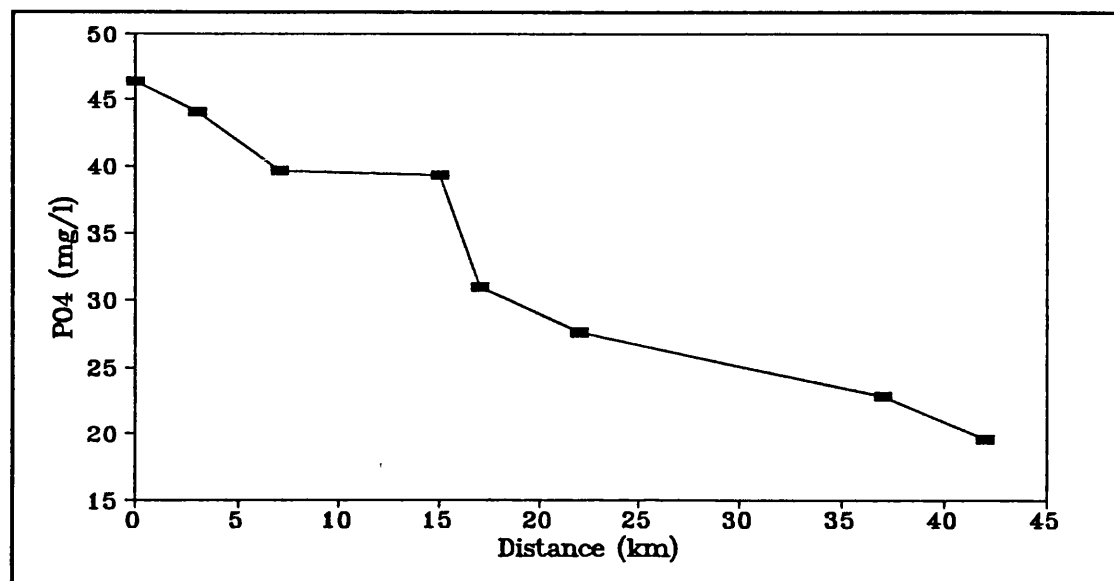


FIGURE 4.5: Orthophosphate variation along the river.

4.2.6- SALINITY AS CHLORIDE, Cl⁻:

Generally, the saturation values of oxygen and nitrogen are reduced by the effect of salinity, which were indicated in the form of chloride concentrations. Concentrations of chloride showed very little change along the river course, (figure 4.6). However, Chloride maintained high levels through out the study period (380-420 mg/l) except during flood times. The River Tigris, Iraq, which falls under the same environmental conditions contains 35-50 mg/l of chloride, (Al-Layla *et al.*, 1989).

4.2.7- TOTAL ORGANIC CARBON (TOC), CHEMICAL OXYGEN DEMAND (COD), AND BIOCHEMICAL OXYGEN DEMAND (BOD₅):

The permanganate value (PV), also known as (TOC), serves as an indication of the potential oxidation processes, being biological or chemical. It is believed that TOC gives more convenient and direct expression than BOD or COD. However, it does not give the same kind of information since BOD is a measure of the oxygen required by bacteria in stabilizing decomposable organic matter.

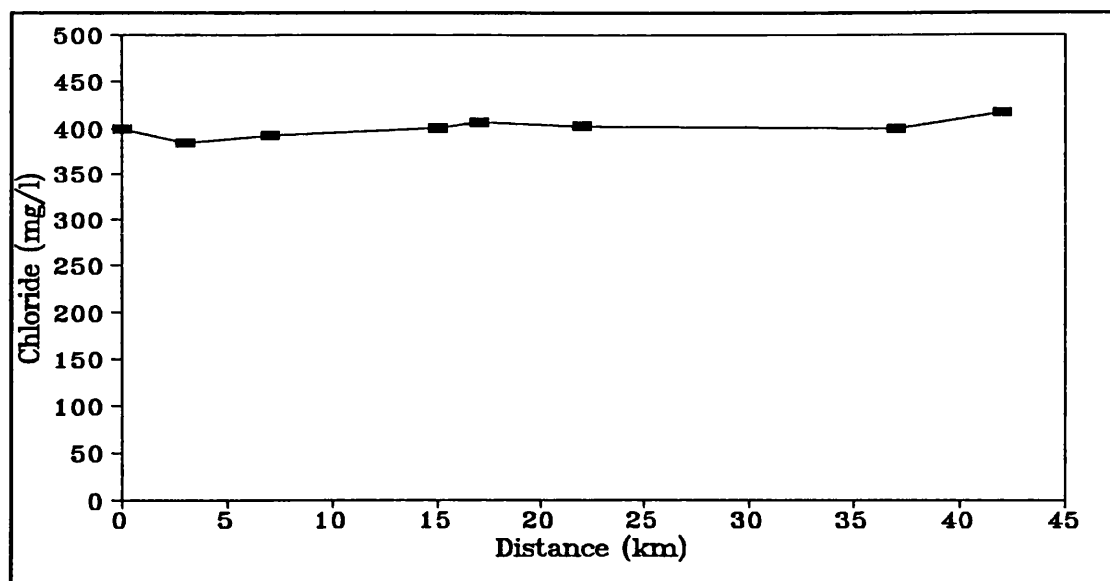


FIGURE 4.6: Variation of chloride along the river.

COD is widely used as a means of measuring the pollutional strength of industrial and domestic wastes. The COD test has a higher precision than the BOD test. BOD₅ usually considered to represent the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions.

Figure (4.7) shows the variation of these parameters along the river course with higher decreasing rates of the chemical oxygen demand than the biochemical demand. This indicates that oxygen is being depleted for the oxidation of chemical matters more than its depletion by microorganisms.

BOD tests were carried out for the standard five-day test and were also incubated for longer periods extended in some cases to 25 days to detect Nitrogenous Oxygen Demand (NBOD), (figure 4.8). Another rise was detected indicating the second stage in the BOD curve, NBOD. However, these values were not much higher than the 5-day BOD, especially down stream of site five which can be attributed to the dilution

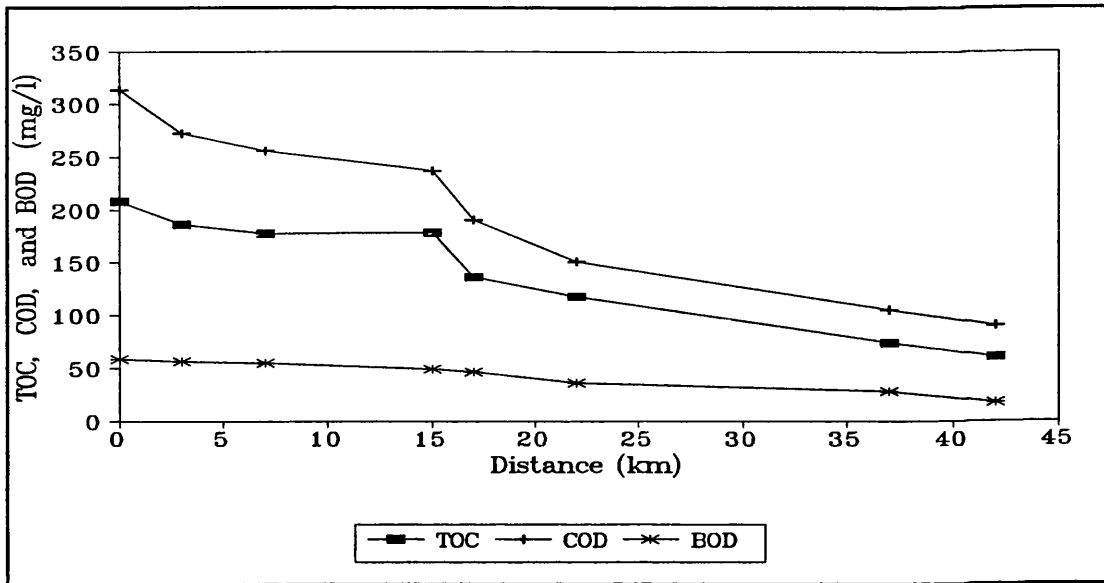


FIGURE 4.7: Variation of TOC, BOD and COD along the river.

effect of the tributary and to the fact that the water down stream is already partial nitrified, hence nitrification and therefore NBOD will be lower. It is also probable that for the sites with a low difference between BOD_5 and NBOD, NBOD started at the same time as the carbonaceous BOD, although nitrification proceeded at a slower rate. Site 5 showed a high NBOD which is attributed to the fact that microorganisms increase in number and activity from site 2 to site 5 where they reach a maximum then start to decrease again due to the decrease in the available oxygen as discussed earlier in figure (4.2). The notable third rise in BOD at site 5 is probably related to the fact that nitrification is a two stage reaction involving two types of microorganisms (*Nitrosomonas europaea* and *Nitrobacter winogradskyi*) which have different activity rates and will result in a faster reaction for the first reaction and a slower one for the second. Moreover, *Nitrobacter winogradskyi* activity (responsible of the second reaction) depends on *Nitrosomonas europaea*, therefore, *Nitrobacter winogradskyi* will increase in activity when a sufficient number of *Nitrosomonas europaea* has been

formed. The third rise in NBOD can also be noticed for sites 3 and 7, however that of site five is clearer due to higher cell concentration.

Figure (4.8) shows the BOD curve for six sites. It is clear that the BOD_5 accounts for most of the total BOD, where a sharp rise, over the first five days, can be seen followed by another rise after around 15 days of the test. The second rise represents the NBOD.

BOD_5 values along the river (figure 4.7) show that the river is undergoing a purification process. Yet, when considering NBOD, the process is disturbed by the high nitrogen content, which explains why BOD values will not necessarily drop sharply along the river course. These values may contain considerable amounts of NBOD which is responsible for the increase in the BOD values in some places along the river course.

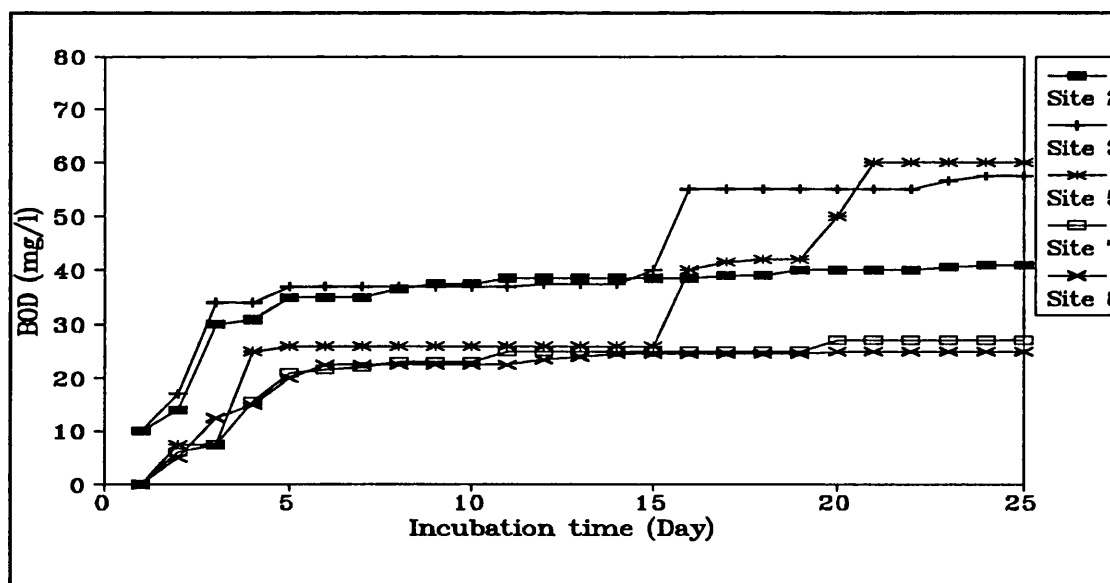


FIGURE 4.8: BOD_5 and ultimate BOD at different sites along the river.

However, the interference caused by nitrifying organisms makes the actual

measurement of CBOD impossible unless prevention is made to eliminate nitrifiers effect. This was actually done for River Zarka by adding to the incubated samples an inhibiting agent, Allyl Thiourea (0.5 g/l $C_4H_8N_2S$).

Figure (4.9) illustrates the difference in BOD_5 , CBOD, and NBOD for sites 2 and 6, these two sites were chosen to represent the River Zarka before and after its confluence with the tributary. It can be seen that NBOD at site 2 is higher than CBOD, while at site 6 CBOD is higher than NBOD. This can be attributed to the fact that the water at site 6 is already partially nitrified with higher oxygen concentrations and lower bacterial and ammonia concentrations than site 2. At site two, although NBOD was higher, nitrification was slow because of the lower oxygen concentrations available and the slow growth rate of nitrifying bacteria. Furthermore, this figure shows that both CBOD and NBOD start within the first days of incubation which explains the small difference between BOD_5 and the total or ultimate BOD shown in figure 4.8.

4.2.8- TURBIDITY:

Light is important in streams, but it may be reduced due to high turbidity. Turbidities more than 30 ftu are high enough to cut off sunshine almost completely except for a shallow layer close to the surface (Arceivala, 1981). Turbidity usually seems to be the major limiting factor in algal growth, (Palmer, 1980).

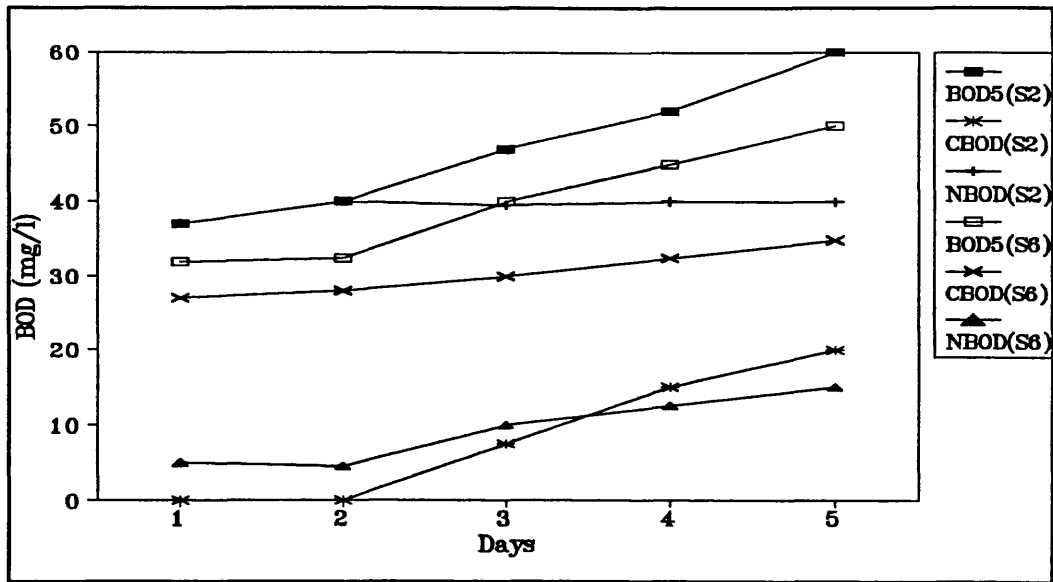


FIGURE 4.9: BOD₅, CBOD and NBOD at sites 2 (plant's effluent) and 6 (after mixing with the tributary).

Figure (4.10) shows turbidity variations along the river course which increases until site 4 and then starts to decrease thereafter. Turbidity of the river increases during wet season due to land flushing. However, since River Zarka is a shallow river with a maximum depth of 65cm and an average velocity of around 0.4 m/s, turbidity has a limited effect.

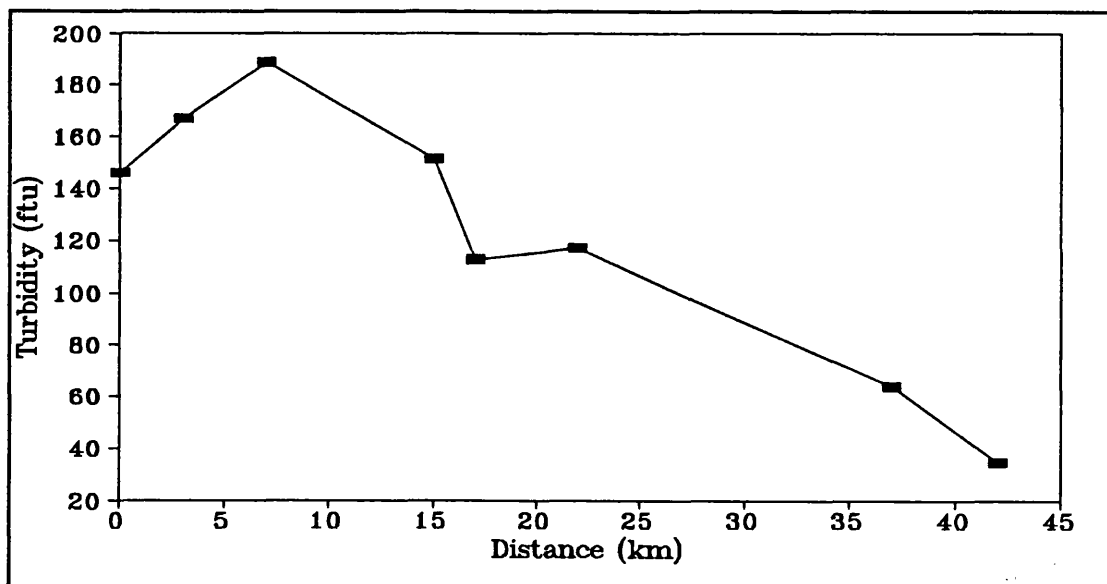


FIGURE 4.10: Variation of turbidity along the river.

4.2.9- HYDROGEN SULPHIDE (H_2S):

The unpleasant odour of the river water especially upstream is an indication of the presence of relatively high amounts of hydrogen sulphide which originated within the pipeline carrying the wastewater from the three cities served by the waste stabilization ponds. Figure (4.11) shows the hydrogen sulphide levels along the river course with a decreasing trend due to aeration. HS can interfere with ammonia determination giving a false value which may explain some discrepancies in reported literature values. Therefore, prior to measuring ammonia concentrations, hydrogen sulphide gas must be stripped off or transformed into a soluble form.

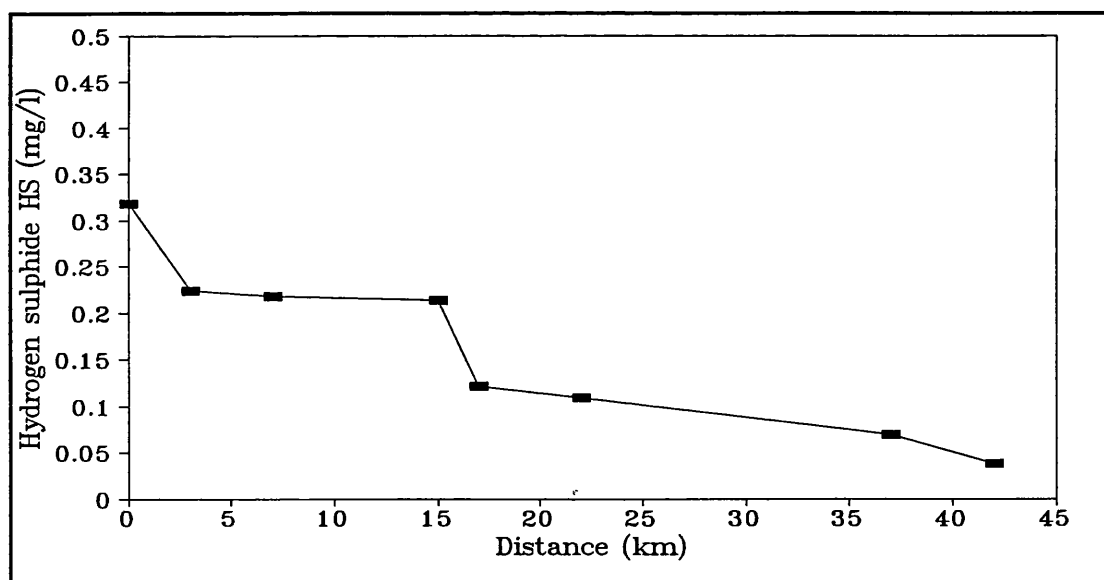


FIGURE 4.11: Hydrogen sulphide variation along the river.

4.2.10- CHLOROPHYLL "a":

Chlorophyll "a" is an algal biomass indicator which represent the requirement of oxygen for respiration, which can be considered to proceed continuously, while production of oxygen by photosynthesis occurs only during the day light.

Chlorophyll "a" concentrations are high at upstream sites and decreases slowly until

after site 6 where the decrease is at a much higher rate, (figure 4.12). The high chlorophyll content in the upstream sites is related to the fact that algae is being produced in the waste stabilization ponds over the retention period of around 40 days within the aerobic lagoons. The speed of the river and its quality as well as high light intensities, prevent algae from building up and cause it to be flushed away hence lower values of chlorophyll are possible downstream. The toxicity of the river water also inhibits the production of algae inspite of the high nutrient concentrations. Algal activity will be discussed in more details in chapter Five.

Light is an important factor for algal growth, but exposure to high light intensities and long sunshine duration can cause an adverse effect on algal biomass leading to what is known as photodestruction of chlorophyll.

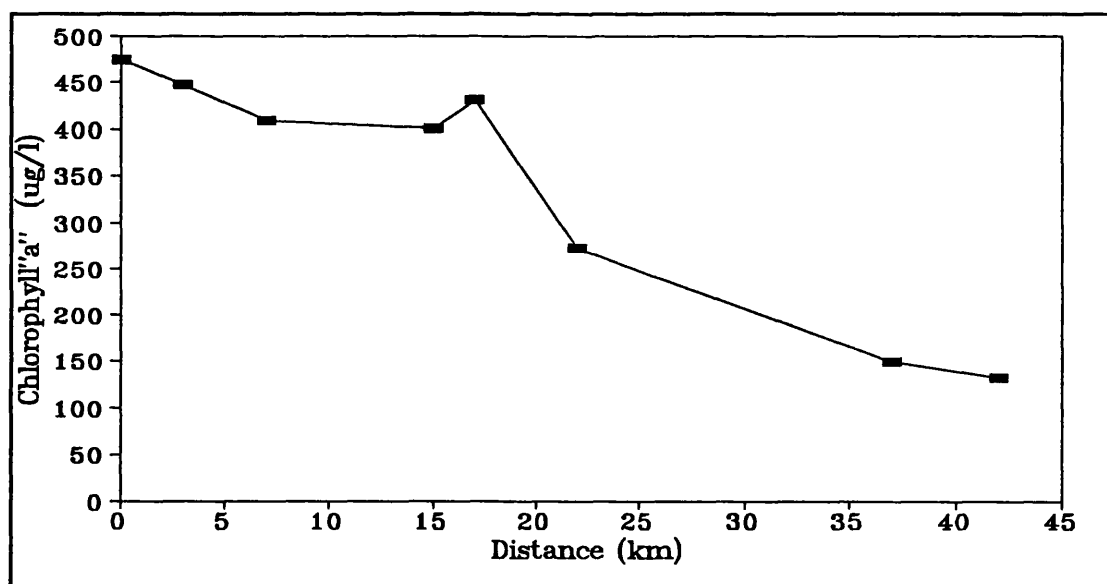


FIGURE 4.12: Chlorophyll "a" concentration variation along the river.

4.2.11- BACTERIAL COUNT:

Bacterial count is represented by cell concentration of total count, *Nitrobacter winogradskyi*, *Nitrosomonas europaea*. and anaerobic bacteria. The high bacterial

content indicates the high oxygen requirement by the river water. Bacterial count starts at low levels due to chlorination of wastewater at the treatment plant and then starts to increase due to oxygenation, yet it starts to die off again due to self purification, (figure 4.13).

Nitrosomonas europaea and *Nitrobacter winogradskyi* are responsible for the conversion of ammonia into nitrite and then into nitrate, respectively. While the anaerobic bacteria are responsible for the denitrification in which nitrate is converted to molecular nitrogen which in turn is lost to the atmosphere.

A set of experiments were carried out to investigate the effect of different cell concentrations on nitrogen transformations, (section 5.4.2) which describes the transformation of the different nitrogen compounds at different cell concentrations. Dilution was made by using sterile river water prepared by autoclaving the sample at 120°C for 20 min.

In figure (4.13) it can be noticed that the total bacterial count is smaller than the sum of the individual counts. This is due to the fact that for the total bacterial count, incubating plates were read within 24-48 hours of incubation, which will not account for the nitrifiers and denitrifiers which needed 2-3 weeks of incubation to have a readable plates (due to their slow generation time which may extend from several hours to several days). The results do however, give an indication of the relative concentration between the two species.

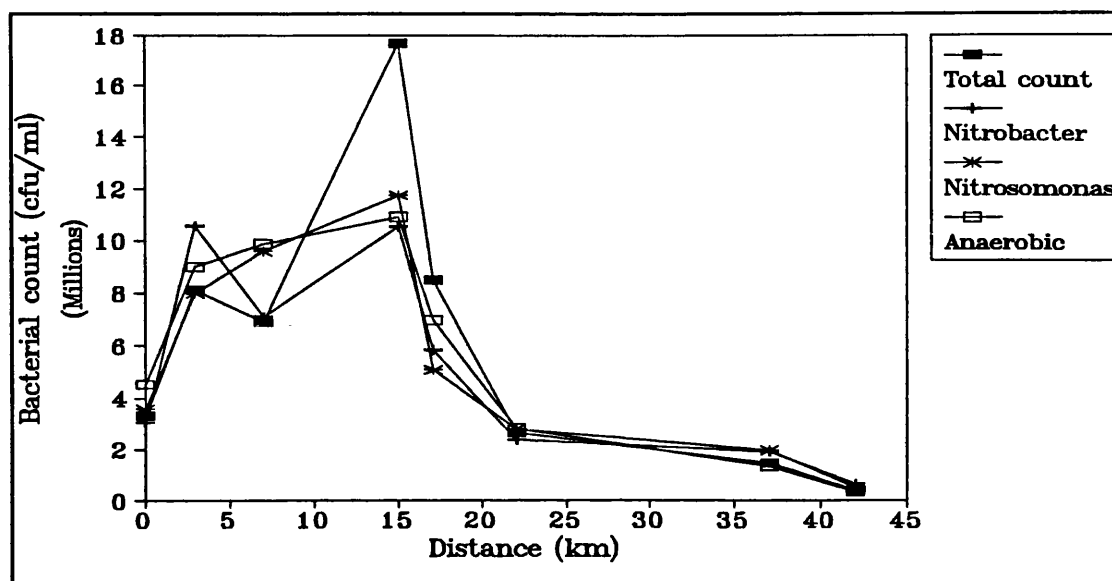


FIGURE 4.13: Concentration of total bacterial count, *Nitrosomonas europaea*, *Nitrobacter winogradskyi* and anaerobic bacteria.

4.3- AL-SUKHNEH STREAM (THE TRIBUTARY) (SITE 10):

Although some industrial and municipal wastes are being discharged into the stream, it is considered as a tributary with less pollutional severity as it originates from fresh water springs. It has low flows during the dry season and almost dry at the end of summer. Flows during the wet season, following a flood are much higher. However, the flow rate of Al-Sukhneh stream is about 10-15% of the wastewater effluent stream originating from the wastewater treatment plant and reaches to 50% over a short period of time during a wet season, (figure 4.14). However, every year during the rainy season and due to runoffs from surrounding areas and from Wadi Dhuleil, the river receives huge floods over short periods of time which does not exceed several hours or at best few days. These annual events causes the sediments at the bottom of the river to be flushed every year and deposits only accumulates during the dry periods.

Figures (4.15) shows the quality difference, in terms of BOD, between the River Zarka

and Al-Sukhneh stream. It is clearly seen that the River Zarka is much more polluted than the tributary, and the quantity of the Zarka is much higher. The low flows of the tributary does not help in diluting the highly polluted river.

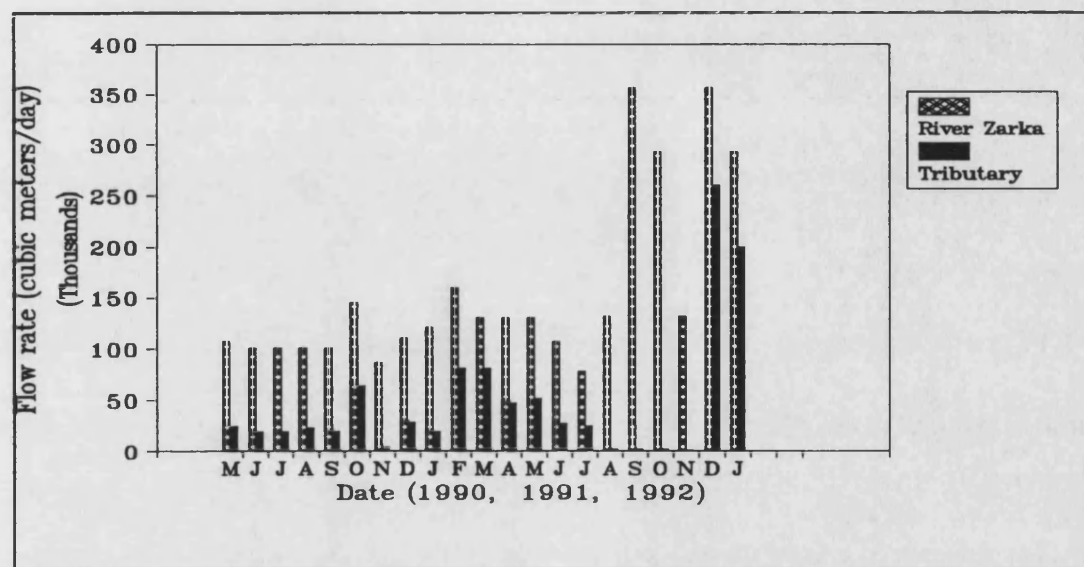


FIGURE 4.14: Flow rates of River Zarka and its tributary over the study period.

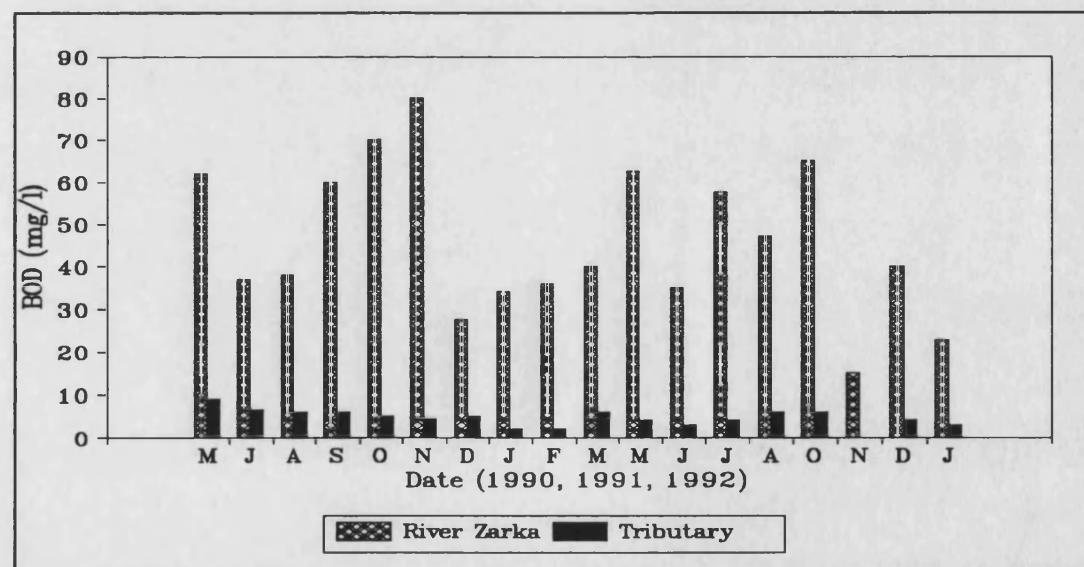


FIGURE 4.15: Quality of River Zarka compared to the quality of the tributary in terms of BOD₅ over the study period.

CHAPTER FIVE

ON-SITE AND LABORATORY BATCH EXPERIMENTS

5-1 INTRODUCTION:

It is important, when formulating a model, that on-site and laboratory experiments are conducted in order to find reaction rates, constants and coefficients. Any model needs correction factors to encompass local temperature variation, inhibition and environmental effects.

It is also important to study other water systems to point out elements of concordance or disagreement in order to better understand the problem, and to make the solution as robust as possible. The nature of a process should be fully investigated to consider the presence and absence of key factors influencing the system.

Therefore, a set of batch experiments were conducted with pure culture, activated sludge effluent, and River Zarka water which is considered to be a semi-treated effluent. These experiments included the following factors:

- different oxygen concentrations,
- different cell concentrations,
- different carbon sources,
- different pure culture incubating media,
- presence and absence of river bed sediments,
- light and dark effects,
- diurnal oxygen and temperature variations,
- settling and resuspension of suspended solids,

- algal and bacterial biomass growth and activity, and
- different incubation temperatures.

5.2- PURE CULTURE EXPERIMENTS:

An understanding of the basic growth kinetics of nitrifying and denitrifying bacteria in pure culture is useful for a number of reasons. It is essential to measure rates of nitrification in the absence of other complicating factors which result from varying environmental conditions and contaminating organisms. The kinetics observed in pure culture are applicable to nitrification in natural environments, often with similar rate constants, and any deviation from standard kinetics highlight therefore the nature of local environmental effects (Prosser, 1990).

Short-term experiments, with incubation times less than the doubling time of the organism, measure activity, while long-term experiments measure growth. Short-term batch experiments, which typically last for several hours, are used to determine kinetic constants and quantitative effects of substrate concentration, inhibitors, etc.. The minimum doubling time reported for nitrifying bacteria varies from 8 hrs (Prosser, 1990), to between half a day and several days, (Huang et al., 1974). Any growth in such experiments will consequently not be significant. Changes in substrate or product concentration therefore, characterize activity rather than growth if incubation times are less than the lag period or the doubling time. However, the denitrifying bacteria *Pseudomonas fluorescens* doubling time is 20 minutes, it was used therefore to measure the influence of substrate concentration on the growth rate of the microorganisms.

Pure cultures of *Nitrobacter winogradskyi* (organisms responsible of transforming nitrite into nitrate), *Nitrosomonas europaea* (transforms ammonium into nitrite), *Alcaligenese xylosoxidans subsp. xylosoxidans* and *Pseudomonas fluorescens* (both responsible of denitrification by transforming nitrate into molecular nitrogen), were incubated in shaker flasks and fermenters in appropriate media as described in section (3.2.2). The selection of these types depended on a study carried out to isolate the most abundant species in River Zarka water, (Khoury, 1986 and WERSC, 1991). When an experiment was performed with these organisms, the overall environment was set to reflect the Zarka system, unless otherwise stated (e.g. when varying oxygen concentration, temperature, or cell concentrations).

The effect of substrate concentration on the bacterial activity was measured by seeding a pure culture of *Pseudomonas fluorescens* with nitrate concentrations in the range 5-40 mg/l, to bring it up to that typical of the River Zarka at all sampling sites and was provided with oxygen concentrations (4-6 mg/l), also as in the Zarka. Figure (5.1) shows that within this range, substrate concentration had no effect on the bacterial activity over the detection period. When this experiment was repeated with different initial concentrations of nitrite and ammonium typical of the Zarka concentrations, the same result was obtained.

Some Pseudomonads are aerobic organisms and extract oxygen from readily available oxygen molecules, while *Pseudomonas fluorescens* which transform nitrate into molecular nitrogen by extracting oxygen from nitrate, are strictly anaerobic. Therefore, at conditions where molecular oxygen is available, these microorganisms cannot

perform the transformation, which was confirmed by their activity in this experiment by no changes in nitrate concentrations.

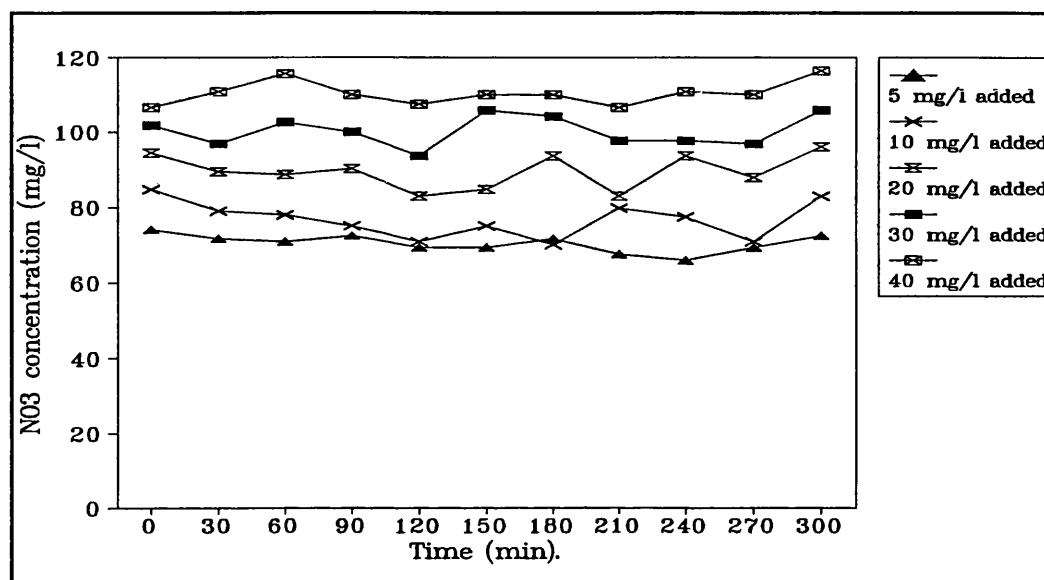


FIGURE 5.1: *Pseudomonas fluorescens* exposed to different concentrations of nitrate at an oxygen concentration of 4–6 mg/l and 25°C.

The activity of *Nitrosomonas europea* (responsible for the transformation of ammonium into nitrite) was followed by measuring substrate and product concentrations over a period extended to more than 35 days (since the doubling time of these microorganisms extends from several hours to several days) at 25°C (a favourable temperature for these organisms and typical of the Zarka). The result was a very slow nitrification process with an ammonium decay rate of $5.0 \times 10^{-4} \pm 6.1 \times 10^{-5}$ mg/l/min, (figure 5.2). The rate was calculated by finding the slope of the best fit straight.

The same experiment was carried out with *Nitrobacter winogradskyi* (responsible for the transformation of nitrite into nitrate) where an even slower process was observed

with a nitrate production rate of $8.3 \times 10^{-5} \pm 2.3 \times 10^{-6}$ mg/l/min, (figure 5.3). The reason behind the slow process is the slow doubling time of the microorganisms and the new environment to which they were subjected.

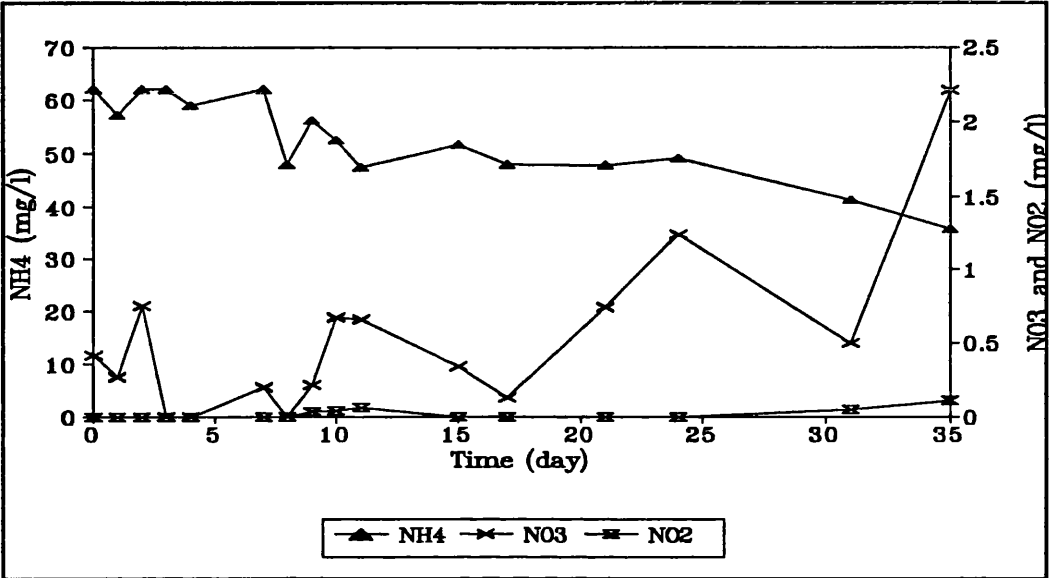


FIGURE 5.2: Changes in N-compounds by *Nitrosomonas europaea* pure culture at 25°C without forced aeration.

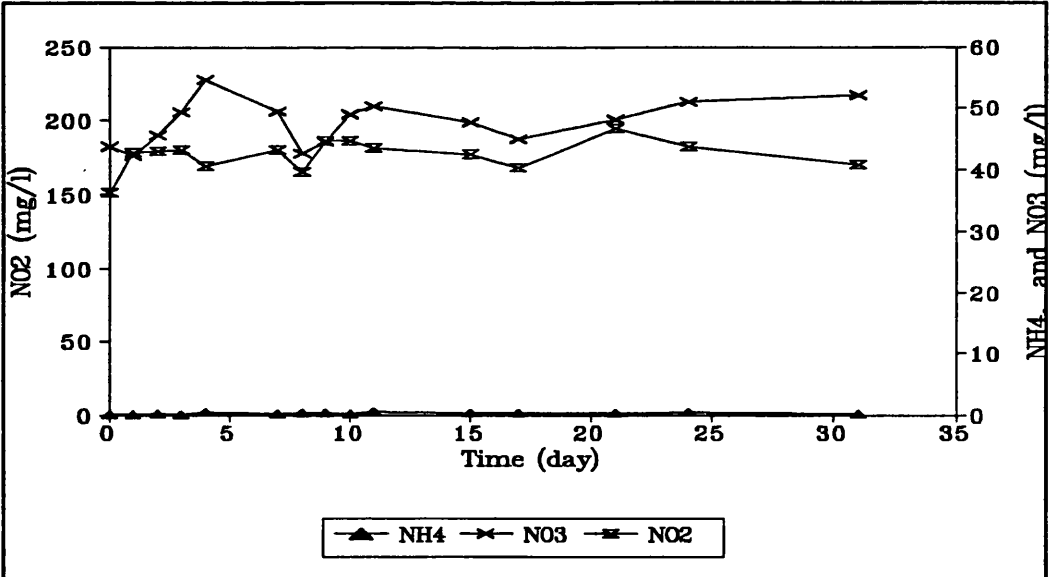


FIGURE 5.3: Changes in N-compounds by *Nitrobacter winogradskyi* pure culture at 25°C without forced aeration.

The behaviour of a mixed culture of *Nitrosomonas europaea* and *Nitrobacter winogradskyi* of equal proportions was then investigated as shown in figure (5.4). The

rates of ammonia decay and nitrate production were 15 times faster than as monocultures, $6 \times 10^{-3} \pm 2 \times 10^{-3}$ mg/l/min and $4.0 \times 10^{-4} \pm 3.9 \times 10^{-5}$ mg/l/min, respectively. This could be credited to some enzymatic or biochemical energy transfer phenomenon existed between the two, a phenomenon beyond the scope of this thesis. Gee *et al.* (1990) investigated the interaction between these organisms and found that increasing *Nitrosomonas europaea* population increased the stability of the *Nitrobacter winogradskyi* population and also increased their activity, but they failed in explaining the reason.

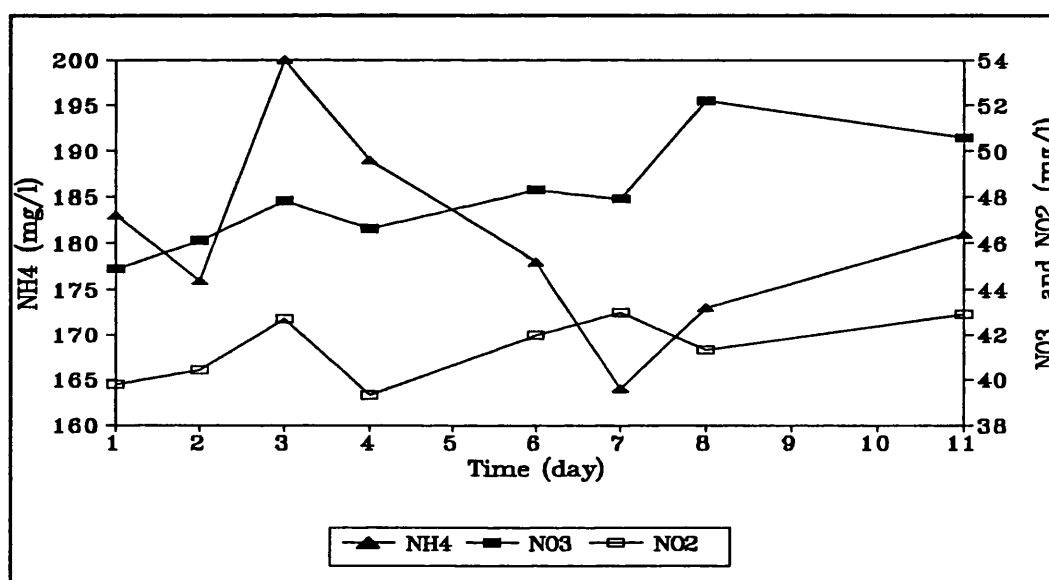


FIGURE 5.4: Changes in N-compounds by a mixed culture of *Nitrosomonas europaea* and *Nitrobacter winogradskyi* at 25°C without forced aeration.

The carbon source can be essential in dictating bacterial growth. The dependence, or otherwise, of the bacteria on the carbon source was investigated by incubating *Pseudomonas fluorescens* in media utilizing three different carbon sources, (acetate, glucose and calcium carbonate). There was no significant difference found in the activity of the bacteria, indicating a high degree of tolerance of these organisms to different carbon sources.

The growth rate of *Pseudomonas fluorescens* (with a doubling time of 20 min), was followed by measuring the optical density of the medium at 480 nm. In this experiment, different concentrations of nitrate were used to investigate the effect of substrate on the growth rate of bacteria over the range found in the River Zarka, and also at concentrations slightly lower and slightly higher (i.e. 15-400 mg/l NO₃). Figure (5.5) shows that over this range, bacterial growth was not affected by nitrate concentration. However, the growth rate (3×10^{-3} - $5 \times 10^{-3} \pm 8 \times 10^{-4}$ day⁻¹) was slow considering the low doubling time for this type of bacteria. Furthermore, the medium containing low nitrate content showed faster bacterial decay since nitrate was exhausted, but if a continuous supply of the same nitrate concentration was available, the bacteria would continue to grow until reaching steady state.

Another experiment was carried out to measure the growth rate of *Pseudomonas fluorescens* incubated in nitrate enriched medium (nutrient broth, 1000 mg/l NO₃), in comparison to a prepared medium containing a nitrate concentration typically found in the Zarka (50 mg/l NO₃). Figure (5.6) shows that the growth rate in nutrient broth (0.3 ± 0.02 day⁻¹) was slightly higher than that in the prepared medium (0.25 ± 0.02 day⁻¹). Growth started earlier and maintained a high constant rate due to the availability of nitrate as an oxygen source, while it took the bacteria more initial time to adapt to the prepared medium (50 mg/l nitrate). They also started to die off earlier as nitrate was used up. The same carbon source, same initial cell concentration and same incubating temperature were used for both media. This indicates that nitrate is essential for the growth of this type of bacteria and it should be available in sufficient amounts to keep high bacterial growth rate, otherwise, nitrate deficiency will result in

delayed growth and earlier bacterial decay.

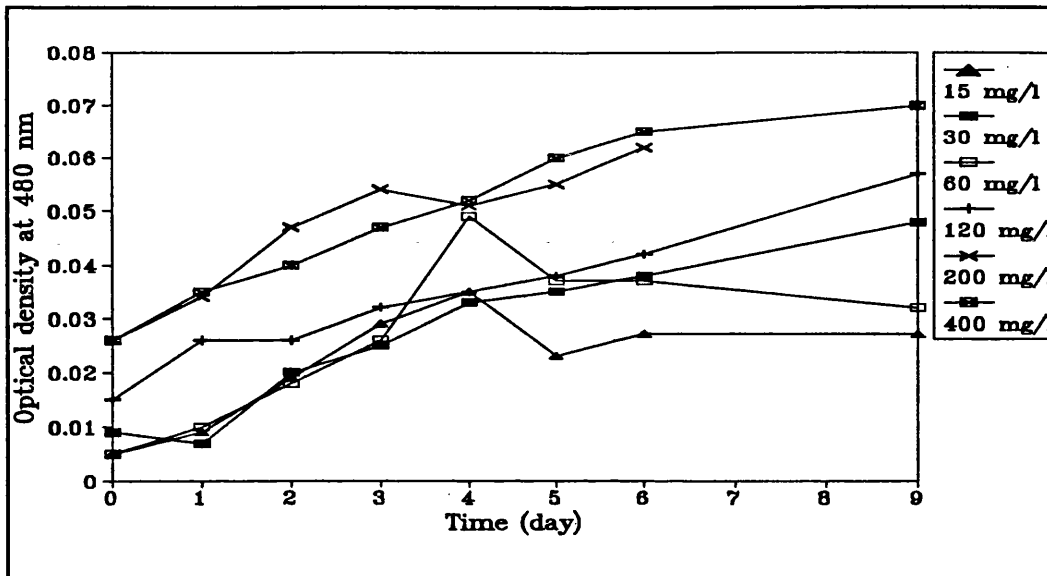


FIGURE 5.5: *Pseudomonas fluorescens* growth curve in media containing different nitrate concentrations at 25°C without forced aeration.

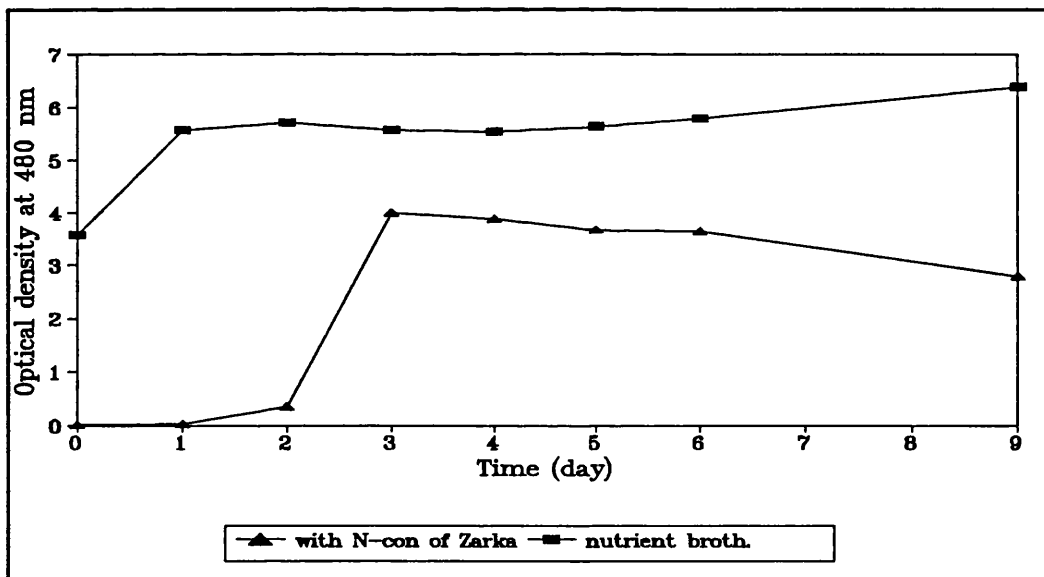


FIGURE 5.6: *Pseudomonas fluorescens* growth curve in nutrient broth and in a prepared medium containing nitrogen concentrations of the Zarka

5.3- ACTIVATED SLUDGE (AS) WASTEWATER EFFLUENT:

Activated sludge (AS) effluent from a Wessex Water Plc. wastewater treatment plant located at Avonmouth, England, was used to carry out batch experiments under the different incubation conditions used for measurements carried out with the River Zarka

water (section 5.4). The aim of these experiments was to investigate similarities or disagreements between activated sludge effluent and the Zarka water as, primarily, Zarka water can be considered to represent a semi-treated wastewater effluent (see chapter 4).

The AS effluent was incubated aerobically by continuously blowing air into the incubating flask and anaerobically by blowing through nitrogen gas to strip out oxygen, (an air trap was used to prevent oxygen from entering the system when sampling). The experimental layout is described in section (3.2). All the following experiments were carried out within 4-6 hrs which was found to be less than the generation time of nitrifiers, therefore any change in nitrogen compounds is due to microorganism activity and not due to their replication.

Different oxygen concentrations were used with an AS effluent sample seeded with the same concentration of ammonium found in the Zarka (100-120 mg/l) at site 2, (the wastewater treatment plant's effluent, and the main continuous source of the river). A standard sample (representing the original AS effluent without the addition of ammonium) was used as a control to the system. Figures (5.7, 5.8, and 5.9) show transformations of nitrate, nitrite and ammonium, respectively, at different oxygen concentrations (0, 3, and 5 mg/l). These figures indicate that increasing ammonium concentration (if other conditions were kept the same) did not affect the initial rates of nitrite and nitrate production and ammonium decay. However with the lower concentrations of nitrate and ammonium (represented by the standard sample), bacterial activity started to be inhibited by substrate deficiency, hence slowing down

the rates.

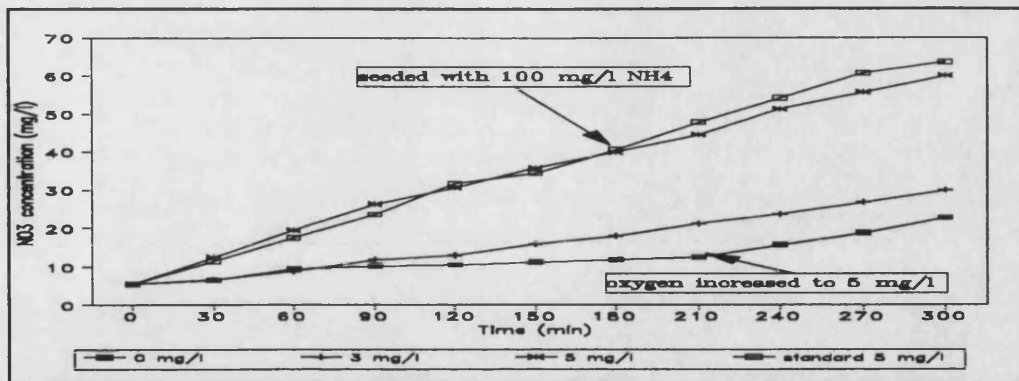


FIGURE 5.7: Nitrate production in an AS effluent seeded with Zarka N-concentration and aerated with different oxygen concentrations at 25°C.

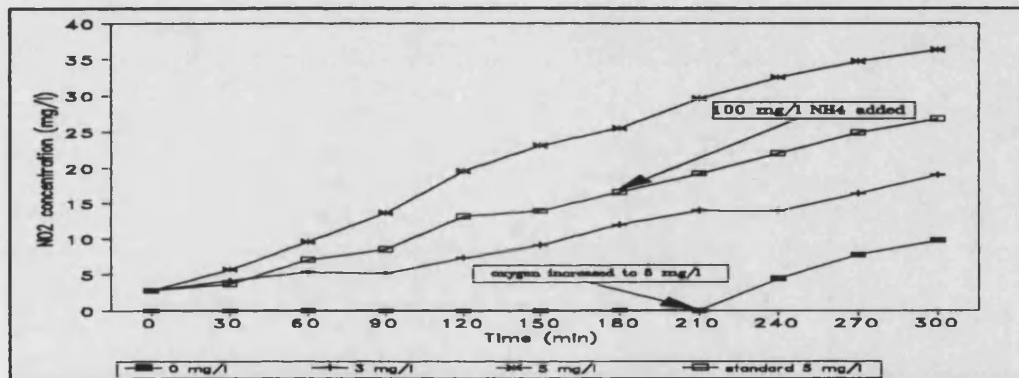


FIGURE 5.8: Nitrite production in an AS effluent seeded with Zarka N-concentrations and aerated with different oxygen concentrations at 25°C.

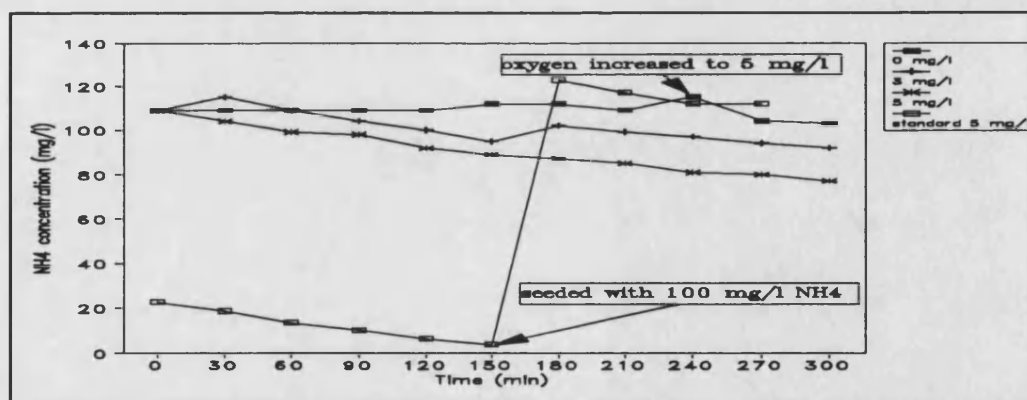


FIGURE 5.9: Ammonium decay in an AS effluent seeded with Zarka N-concentrations and aerated with different oxygen concentrations at 25°C.

A mass balance over the nitrogen compounds in the experiment represented in figures (5.7, 5.8 and 5.9) indicates that the initial nitrogen of 86.05 mg/l as N yielded 83.21

mg/l as N after 300 min. indicating that most of the ammonium which was consumed had transformed into nitrite and nitrate. The difference may be accounted for by some of the nitrogen going into production of bacterial cells. The overall reaction represent the stoichiometric equivalence between ammonium and nitrate. The difference of 0.03% may be attributed to the fact that the experiment was not left for complete nitrification and to the production of bacterial cells.

To examine whether that nutrient deficiency (lack of ammonium) is the reason, the standard sample was supplemented with 100 mg/l NH_4 after 180 min.. The rate was consequently increased to a level slightly lower than that which initially took place (from 0.2 to 0.18 mg/l/min) since the effect is not spontaneous (figure 5.7). The low difference between the two rates is not significant enough especially in the River Zarka where nitrogen compounds are always in excess.

Increasing the amount of oxygen increased the rates. However, it appears that a minimum concentration of around 3-4 mg/l of oxygen was necessary for nitrification to take place, in agreement with the value reported by Arceivala (1981).

When the sample initially supplied with zero mg/l oxygen was subjected to a higher oxygen concentration (5 mg/l), nitrification did become faster with rates of ammonium decay and nitrate and nitrite production similar to other samples subjected initially to high oxygen concentration. The slight difference in the rates could be attributed to the time needed for adaptation. Table (5.1) shows ammonium decay and nitrate production rates at different oxygen concentrations.

TABLE 5.1: Nitrate production and ammonium decay rates of AS effluent at different oxygen concentrations.

	0 mg/l O ₂	3 mg/l O ₂	5 mg/l O ₂	Control standard 5 mg/l O ₂
NO ₃ rate mg/l/min	0.04 ± 5x10 ⁻³ 0.11*	0.08 ± 3x10 ⁻³ -	0.18 ± 5x10 ⁻³ -	0.20 ± 5x10 ⁻³ -
NH ₄ rate mg/l/min	-0.02 ± 6x10 ⁻³ -0.10*	-0.07 ± 6x10 ⁻³ -	-0.10 ± 5x10 ⁻³ -	-0.13 ± 4x10 ⁻³ -

* after increasing oxygen concentration to 5 mg/l.

The AS effluent was then seeded with different concentrations of nitrate (25-100 mg/l, typical of the Zarka content at the different sites), a high concentration of ammonium (200 mg/l to avoid any possible limitation by ammonium deficiency) and aerated to a high oxygen concentration (7 mg/l), to examine whether the type of substrate, e.g. nitrate or ammonium, affects nitrification or the substrate concentration. Production of nitrate, as an indication of nitrification, proceeded at the same rates (0.46-0.51 ± 2.5x10⁻² mg/l/min) for the different concentrations, indicating that substrate concentration as well as substrate type (since the previous experiment showed that ammonium concentration did not affect the rate) had no effect on nitrification rate over the range of interest, (figure 5.10).

A standard sample was used as a control to the system (the original activated sludge effluent without any nitrate addition). The standard sample which contained around 20 mg/l nitrate followed the same trend of nitrate production of other samples. However, when the oxygen supply was cut off from the standard sample, nitrification stopped almost immediately. This again indicates that oxygen is essential for nitrification, and nitrate concentrations over the studied range have no significant

effect on the rate.

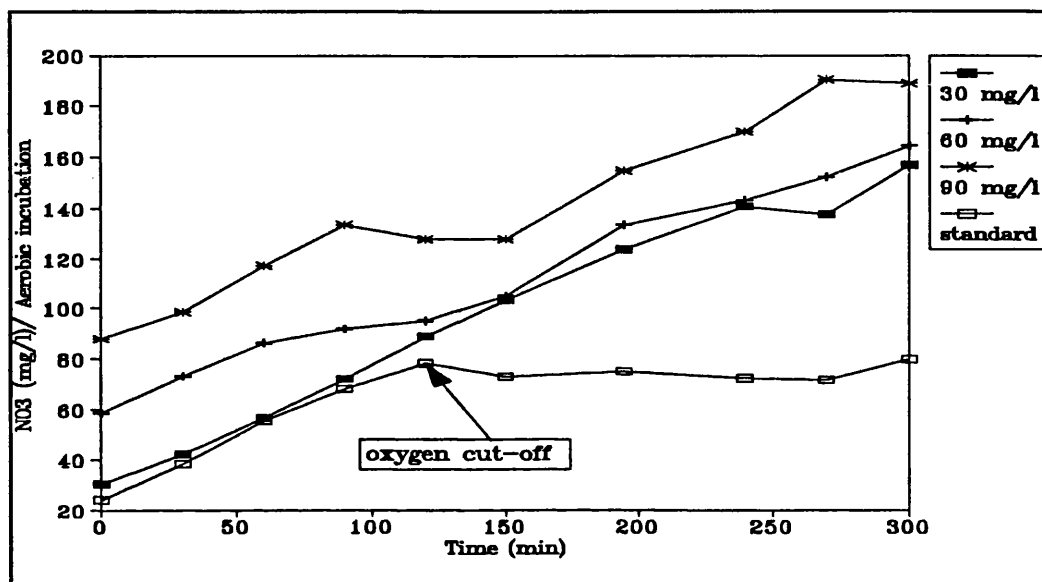


FIGURE 5.10: Production of nitrate in an AS effluent incubated aerobically and exposed to different nitrate concentrations at 25°C.

In agreement with this work, Gee *et al.* (1990) found that the substrate inhibition constant for ammonia oxidation is large (9000 mg-N/l ammonia) using Monod kinetics. Other researchers have made the same conclusion (Huang *et al.*, 1974; and Wild *et al.*, 1970). However, nitrification could be inhibited by substrate concentrations if they are in the form of free ammonia and free nitrous acid (Prosser 1990). Free ammonia can be found only in alkaline medium, i.e. pH above 8.0, while the pH of the Zarka water is always below 8.0 (see section 4.2.1).

Similar samples were incubated anaerobically, to limit the oxygen availability to that provided by nitrate (Figure 5.11.a). Nitrate at the higher concentrations (50-100 mg/l) fell once the bacteria started to utilize nitrate for growth (after a lag period of around 100 min.), and ammonium started to accumulate (figure 5.11.b). While for the samples with low concentrations of nitrate (10-25 mg/l), no change was detected, probably

because of the limited amount of nitrate to be used as oxygen source, and that the bacteria needed more time to start utilizing low nitrate quantities (extending the lag period behind the duration of the experiment). The standard sample (the AS effluent without any nitrate addition with a concentration of around 20 mg/l NO_3), was used as a control and showed the same behaviour as the samples with low nitrate concentrations of 10-25 mg/l.

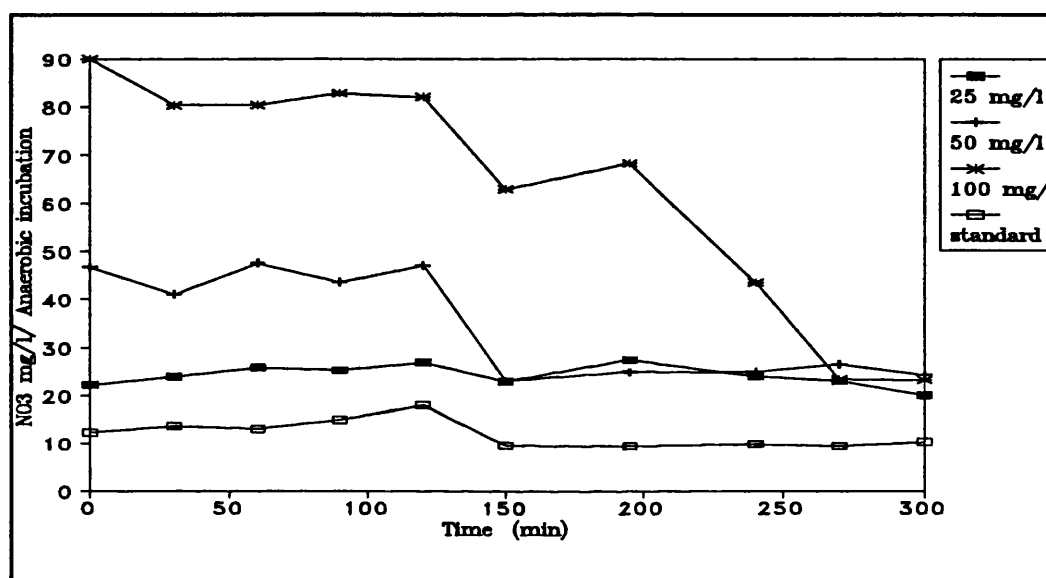


FIGURE 5.11.a: Nitrate production of an AS effluent incubated anaerobically and exposed to different nitrate concentrations at 25°C.

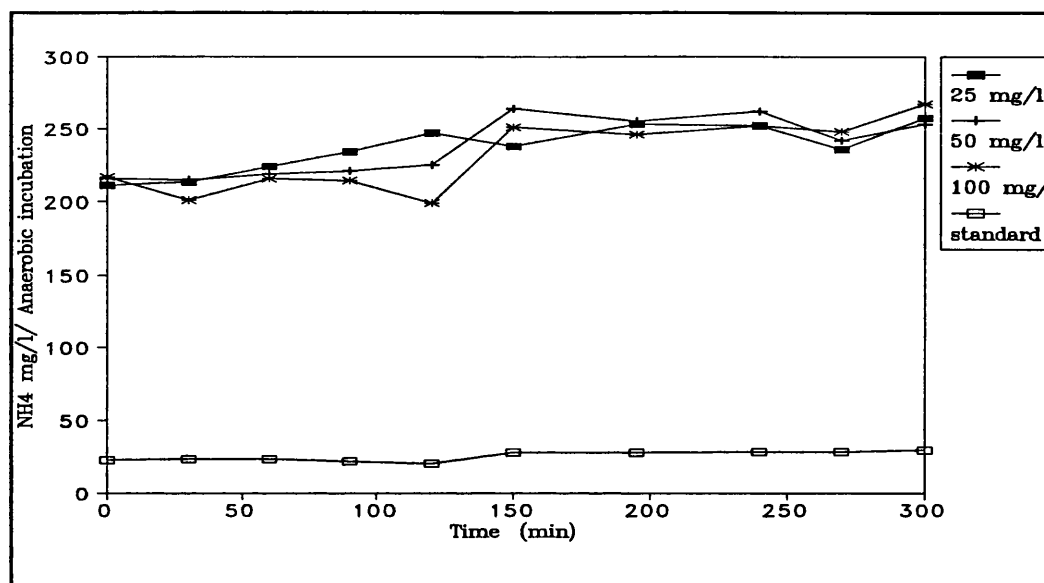


FIGURE 5.11.b: Ammonium accumulation of an AS effluent incubated anaerobically and exposed to different nitrate concentrations at 25°C.

The temperature effect on nitrification using activated sludge effluent was investigated by incubating the effluent with different ammonium concentrations at different temperatures (15, 20, and 25°C, $\pm 1^\circ\text{C}$), representing the River Zarka temperatures at different seasons. Nitrification was clearly affected by temperature, with the rate increasing with temperature, (figures 5.12, 5.13, and 5.14). Table (5.2) shows nitrate production and ammonium decay rates at different temperatures for different initial ammonium concentrations. It is clear that the concentration of ammonium did not affect the rate, while the temperature did. The mathematical expression describing the relationship between temperature and nitrification rates will be discussed in section 5.4.1. A mass balance on nitrogen compounds as N showed that the initial total amount of 75 mg/l N yielded after 300 minutes 73.3 mg/l N which indicates that most of the ammonium was transformed into nitrite and nitrate, but some may have been consumed in production of bacterial cells. It is also noted that the difference in the amount of reactants and products is more at higher temperature due to higher bacterial cells produced.

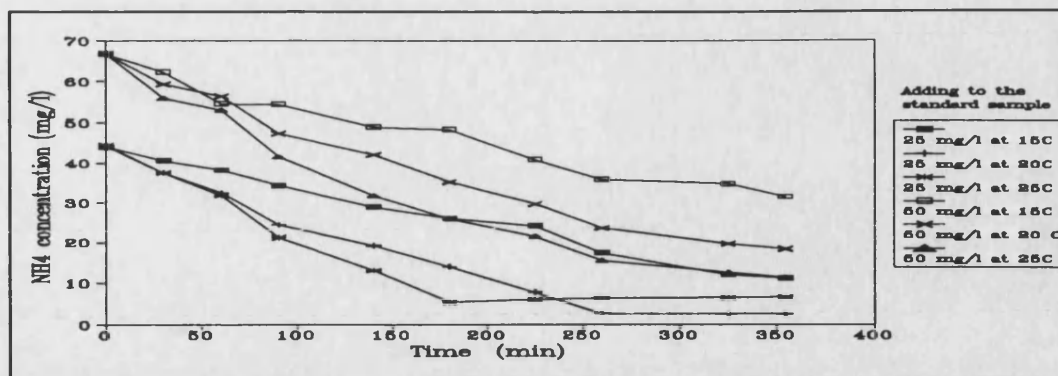


FIGURE 5.12: Ammonium decay of an AS effluent exposed to an addition of 25 and 50 mg/l ammonium concentrations at different temperatures.

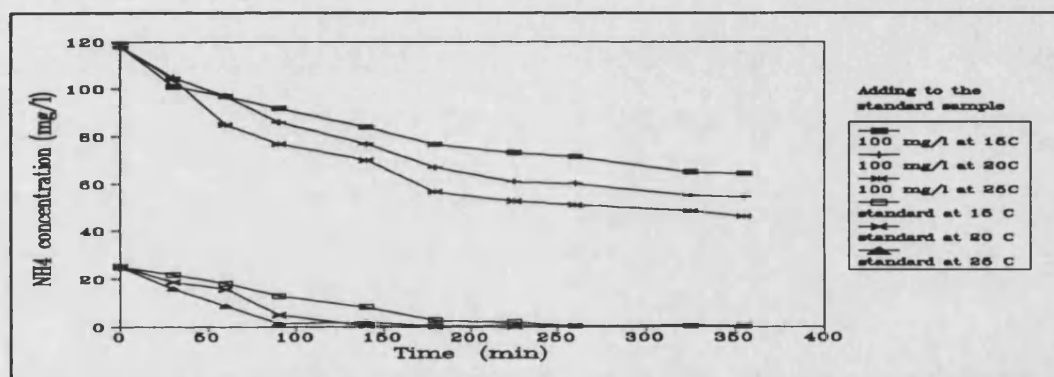


FIGURE 5.13: Ammonium decay in an AS effluent exposed to an addition of 100 mg/l ammonium at different temperatures compared to the original sample.

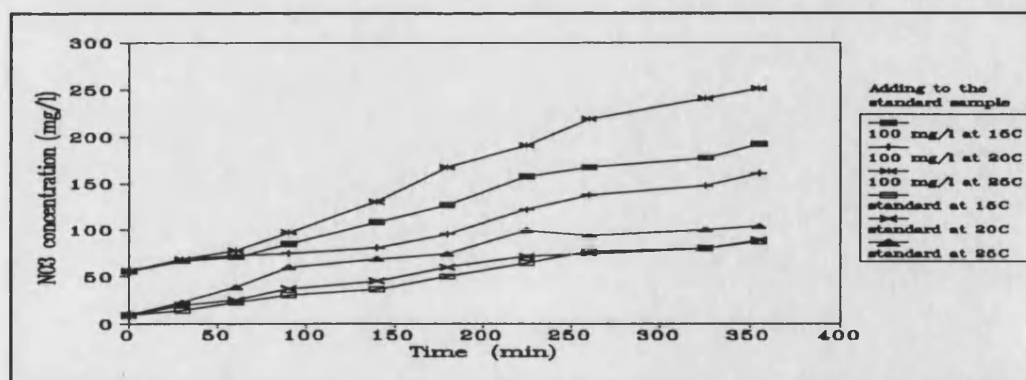


FIGURE 5.14: Nitrate production of an AS effluent exposed to an addition of 100mg/l ammonium at different temperatures compared to the original sample.

TABLE 5.2: Ammonium decay and nitrate production rates at different temperatures for different initial ammonium concentrations.

Ammonium concentration (mg/l)		NH ₄ decay rate mg/l/min	NO ₃ production rate mg/l/min
25mg/l	at 15°C	-0.15 ± 0.006	0.10 ± 0.015
	at 20°C	-0.20 ± 0.010	0.27 ± 0.030
	at 25°C	-0.21 ± 0.004	0.47 ± 0.030
50mg/l	at 15°C	-0.15 ± 0.021	0.11 ± 0.016
	at 20°C	-0.17 ± 0.005	0.25 ± 0.020
	at 25°C	-0.23 ± 0.015	0.49 ± 0.024
100mg/l	at 15°C	-0.15 ± 0.004	0.12 ± 0.022
	at 20°C	-0.19 ± 0.065	0.25 ± 0.020
	at 25°C	-0.22 ± 0.050	0.48 ± 0.021
standard control	at 15°C	-0.13 ± 0.002	0.12 ± 0.008
	at 20°C	-0.16 ± 0.015	0.27 ± 0.010
	at 25°C	-0.21 ± 0.027	0.48 ± 0.027

To account for cell concentration variation, an experiment was carried out by diluting the effluent to lower cell concentrations using filtered effluent (0.3 µm filter, to remove bacteria). The initial bacterial concentration was 2×10^8 cfu/ml. Samples were seeded with River Zarka concentrations of nitrogen compounds (95 mg/l NH₄, 45 mg/l NO₃, and 8 mg/l NO₂ sterilized to prevent possible contamination). Figures (5.15, 5.16, and 5.17) show cell concentration effect on nitrification, where it can be seen that increasing cell concentration increased nitrification, i.e. with higher cell concentration of bacteria, nitrification is faster.

The standard sample used as a control (the AS effluent without cell dilution and without any seed of N-compounds), shows typical nitrification behaviour by which ammonia is oxidized into nitrite and then into nitrate, hence nitrate is being continuously produced, (figure 5.15), and ammonium is being oxidized (figure

5.17) show cell concentration effect on nitrification, where it can be seen that increasing cell concentration increased nitrification, i.e. with higher cell concentration of bacteria, nitrification is faster.

The standard sample used as a control (the AS effluent without cell dilution and without any seed of N-compounds), shows typical nitrification behaviour by which ammonia is oxidized into nitrite and then into nitrate, hence nitrate is being continuously produced, (figure 5.15), and ammonium is being oxidized (figure 5.17). When all of the ammonium had been exhausted, nitrite started to be oxidized (figure 5.16), which explains the fall in nitrite concentrations after initial production. This also explains the occurrence of a peak followed by a decrease in nitrite concentrations for the other curves in figure (5.16).

The standard sample curve fell faster since the initial concentrations of ammonium, nitrate and nitrite were low (20, 18, and 6 mg/l, respectively), while for the other samples the concentrations were 95, 45, and 8, respectively. This does not mean that initial concentrations affect nitrification, but that ammonium (producing nitrite) was depleted. Immediately after the depletion of ammonium, nitrite started to be depleted (since there is no other source to produce nitrite) to form nitrate which continued to be formed, and probably if the duration of the experiment was extended, nitrate would have reached a plateau. However, the initial rates of ammonium decay and nitrate production for the standard sample are the same for the undiluted sample of the same cell concentration as can be seen from table (5.3), which illustrates ammonium decay and nitrate production rates at different cell concentrations. The mathematical relationship between cell concentration and rates of nitrate production and ammonium decay will be discussed in section 5.4.2.

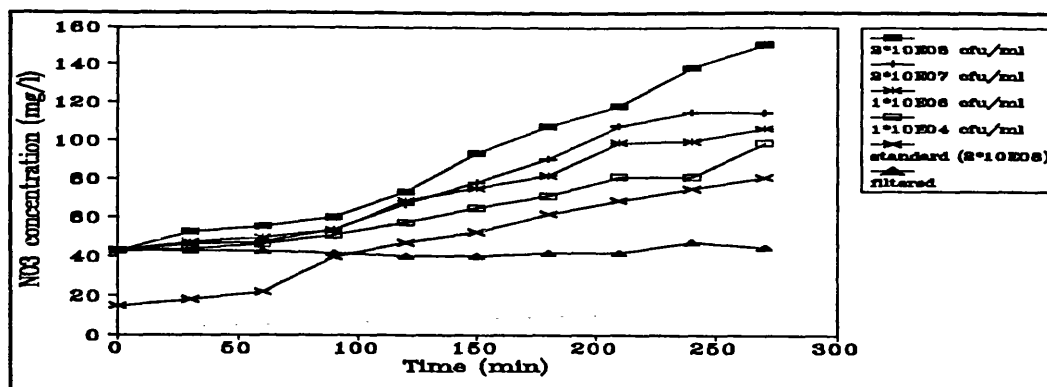


FIGURE 5.15: Production of nitrate of AS effluent at different cell concentrations at 25°C.

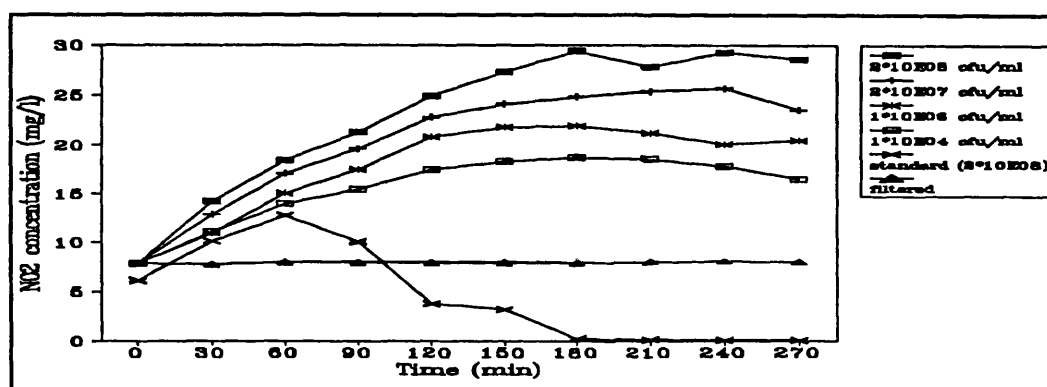


FIGURE 5.16: Changes in nitrite concentration of AS effluent at different cell concentrations at 25°C.

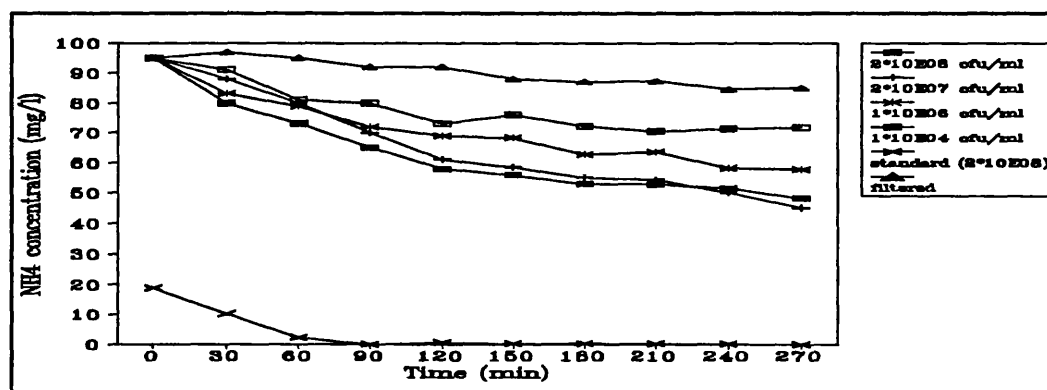


FIGURE 5.17: Ammonium decay of AS effluent at different cell concentrations at 25°C.

TABLE 5.3: Nitrate production and ammonium decay rates at different cell concentrations of AS effluent incubated at 25 °C with 7 mg/l oxygen concentration.

Cell concentration (cfu/ml)	NO ₃ production rate (mg/l/min)	NH ₄ decay rate (mg/l/min)
2x10 ⁸	0.51 ± 0.022	-0.25 ± 0.005
2x10 ⁷	0.37 ± 0.031	-0.25 ± 0.005
1x10 ⁶	0.29 ± 0.061	-0.16 ± 0.040
1x10 ⁴	0.25 ± 0.016	-0.07 ± 0.010
1x10 ⁰	0.005 ± 0.0001	-0.05 ± 0.005
control (2x10 ⁸)	0.50 ± 0.020	-0.27 ± 0.007

5.4- RIVER ZARKA WATER:

In order to find the different reaction rates and constants specific to River Zarka, a set of experiments were carried out by incubating river water from the Zarka at different conditions, as described in the following sections. The initial incubation conditions at which all samples were treated (unless otherwise stated) are:

- continuous oxygen supply controlled at $7.0 \text{ mg/l O}_2 \pm 0.2$ through out the experiment duration by adjusting the aeration rate,
- at a temperature of $25^\circ\text{C} \pm 1^\circ\text{C}$,
- under light without river bed sediment,
- without sample filtration,
- for a duration of 5-6 hours,
- at a pH of 7.8 ± 0.2 , and
- carried out in the laboratory.

5.4.1- EFFECT OF TEMPERATURE:

The same range of temperatures over which the activated sludge effluent was incubated, was used in this experiment (15, 20, and $25 \pm 1^\circ\text{C}$). This range was chosen as representing average temperatures during the different seasons. Figures (5.18, 5.19, and 5.20) show the effect of temperature on the production of nitrate, nitrite, and the decay of ammonium at site 2 (the wastewater treatment plant effluent, main source of the river which may be similar to AS effluent).

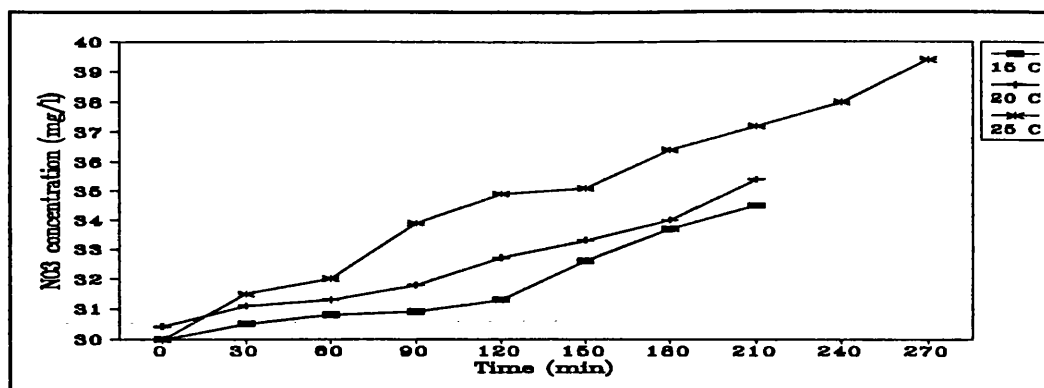


FIGURE 5.18: Nitrate production of the Zarka water at different temperatures at site 2.

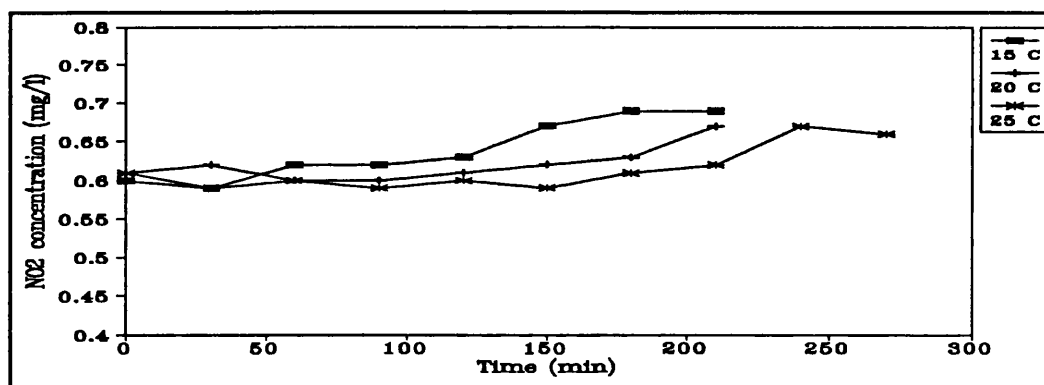


FIGURE 5.19: Nitrite change of the Zarka at different temperatures at site-2.

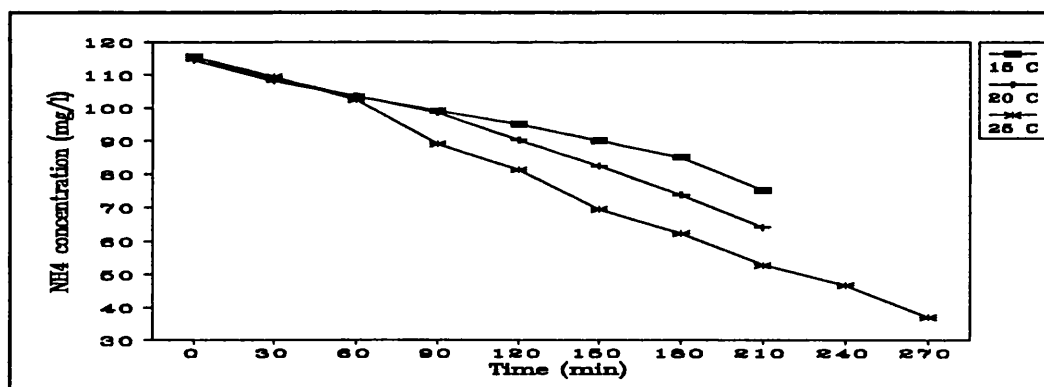


FIGURE 5.20: Ammonium decay of the Zarka at different temperatures at Site-2.

The same experiment was carried out for other sites and showed the same trends. This indicates that the effect of temperature is independent of the water quality (providing that they are treated under the same conditions of oxygen content and cell concentration), i.e. both the activated sludge effluent (discussed in the previous

sections) and the river water at all sites, followed the same trend with increase in temperature (although at different rates). For example, over the temperature range (15-25°C) the nitrate production rate (r_2) of AS ranged between 0.10 ± 0.015 and 0.49 ± 0.024 mg/l/min, while the Zarka nitrate production rate ranged between 0.01 ± 0.003 and 0.06 ± 0.005 mg/l/min. Ammonium decay rate (r_1) was $0.13-0.23 \pm 0.015$ mg/l/min and $0.13-0.48 \pm 0.02$ for AS and the Zarka water, respectively. Table (5.4) illustrates nitrate production and ammonium decay rates at different temperatures along the river.

TABLE 5.4: Rates of ammonium decay and nitrate production of the River Zarka at different temperatures at selected sites along the river.

Site	Temperature °C	NO ₃ (r_2) production rate (mg/l/min)	NH ₄ (r_1) decay rate (mg/l/min)
2	15	0.01 ± 0.003	-0.20 ± 0.008
	20	0.02 ± 0.002	-0.29 ± 0.010
	25	0.04 ± 0.002	-0.31 ± 0.010
5	15	0.02 ± 0.003	-0.36 ± 0.010
	20	0.03 ± 0.003	-0.40 ± 0.010
	25	0.04 ± 0.003	-0.48 ± 0.020
6	15	0.03 ± 0.003	-0.13 ± 0.005
	20	0.04 ± 0.003	-0.15 ± 0.008
	25	0.06 ± 0.005	-0.17 ± 0.010

Crabtree *et al.*, (1986) described the mathematical relationship between temperature and nitrification rates in the Qual 2EU model as follows:

$$k_T = k_{20} * \theta^{(T-20)} \quad (5.1)$$

where:

k_T = rate of ammonium decay or nitrate production at temperature T°C

k_{20} = rate of ammonium decay or nitrate production at 20°C

θ = temperature correction factor

T= temperature in °C.

This basic equation describes the temperature effect found from this work, and the correction factor θ of 1.047 does apply to the Zarka system and to the AS effluent, however with higher standard deviation. Qual 2EU uses the same correction factor for both, the ammonium decay and nitrate production rates (r_1 and r_2). It is found here that a correction factor of $1.118 \pm 3.4 \times 10^{-4}$ and $1.035 \pm 3.8 \times 10^{-3}$ better represent nitrate production and ammonium decay rates, respectively for both the Zarka system and the AS effluent, however with higher standard deviation for AS where $\theta_{r_2} = 1.118 \pm 0.009$ and $\theta_{r_1} = 1.035 \pm 0.002$, respectively as can be seen in tables (A1.1 and A1.2) in the appendix. The level of confidence (in terms of the standard deviation) using Qual 2EU factor is significantly less, especially for nitrate production (standard deviation of 0.111), while it is reasonably similar for ammonium decay (0.003). The tables in the appendix illustrate actual and modelled values using both the Qual 2EU and the Zarka correction factors and the confidence levels using both models. Yongming (1988) found even a higher temperature coefficient (1.150) for ammonium oxidation rate for the Toujiang river.

A mass balance over the nitrogen compound indicated that at higher temperature the nitrogen consumed in the production of bacterial cells appeared higher than at lower temperatures. This is likely since the temperature of 25°C is more favorable for the production of bacteria. At 25°C the loss in nitrogen was 5% while at 15°C it was 2%.

Temperature also affected the deoxygenation of the river water, as can be seen from figure (5.21) which shows deoxygenation at site 6 (selected due to higher active bacterial content after natural dechlorination, see section (5.4.4)). The oxygen concentration of the samples was brought up to 6 mg/l (typical of *in situ*) and they were incubated at different temperatures. Oxygen consumption was then measured by following the decrease in oxygen concentration over the following 1-2 hours. It was found that the higher the temperature, the faster deoxygenation (i.e. rates of $0.016 \pm 3 \times 10^{-4}$, $0.026 \pm 6 \times 10^{-4}$, and $0.033 \pm 9 \times 10^{-4}$ mg/l/min at 15, 20, and 25°C, respectively). This again indicates the effect of temperature on the oxygen demand, with nitrification as being part of this demand. The temperature effect on the deoxygenation rate can be described by using equation (5.1), with a θ of $1.061 \pm 1.5 \times 10^{-5}$.

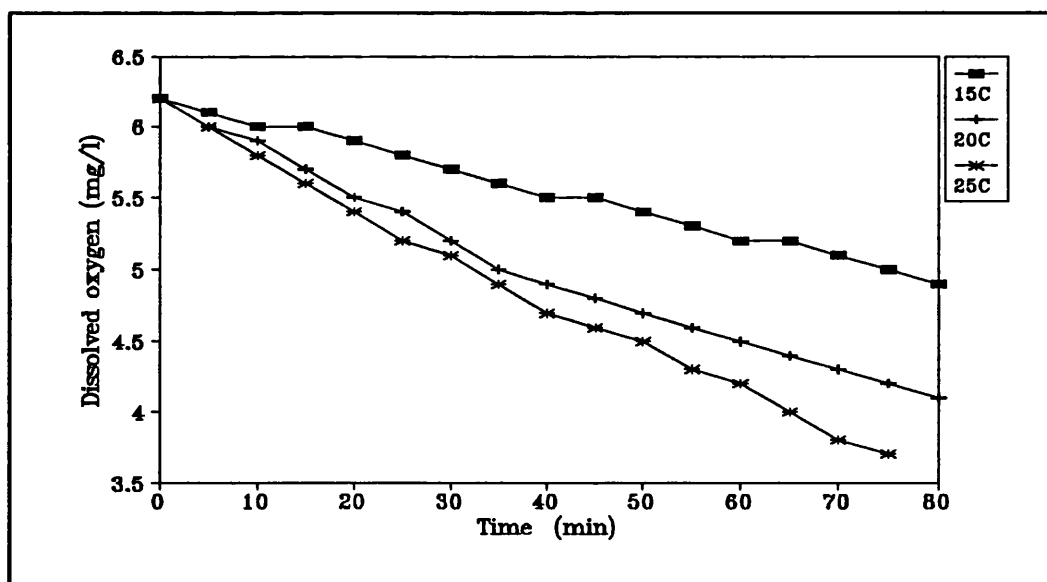


FIGURE 5.21: Deoxygenation at site 6 of the Zarka for un-aerated sample at different temperatures.

5.4.2- EFFECT OF CELL CONCENTRATION:

The effect of variation in cell concentration is better represented if studied with microorganisms from the same water under the study. Therefore, the microorganisms

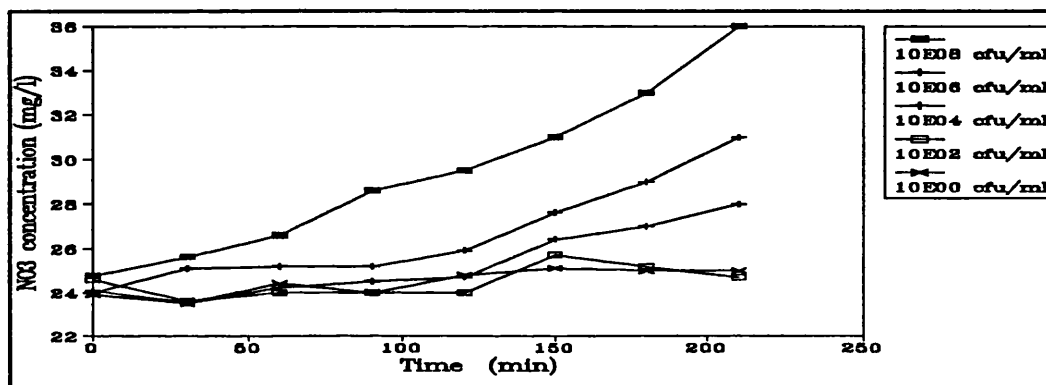
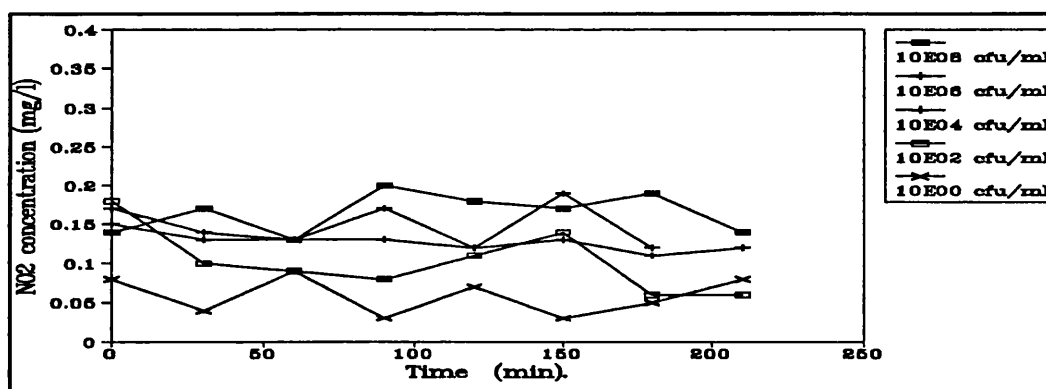
present in the Zarka water were used for this purpose as they best represent the actual environment. Cell concentration was represented by the total bacterial count.

A river water sample from site 5 (chosen to minimize any possible effect due to chlorination, but before the river joins the tributary) was sterilized by autoclaving at 120°C for 15 min. and used as a diluting solution for other samples to test the effect of cell concentration on nitrification. This was done to keep all other water constituents as the undiluted sample so as to minimize any nutrient deficiency (another experiment was also carried out using filtered samples, as with the activated sludge effluent experiments, and was found to show the same effect).

The production of nitrate and the decay of ammonium rates (r_2 and r_1) were affected by the decrease in cell concentration as illustrated in figures (5.22, 5.23, and 5.24) and in table (5.5). Again, this agrees with the activated sludge effluent experiments where in both systems nitrification was reduced as cell concentration decreased. However, due to the unstable nature of nitrite as an intermediate product, the effect on the production of nitrite was not so evident (also the detected concentrations of nitrite at this site were low, at 0.2 mg/l).

TABLE 5.5: Nitrate and ammonium rates at 25 °C for different cell concentrations at site 5.

Cell concentration (cfu/ml)	NO ₃ production rate (r_2) (mg/l/min)	NH ₄ decay rate (r_1) (mg/l/min)
1×10^8	0.07 ± 0.004	-0.40 ± 0.040
1×10^6	0.06 ± 0.003	-0.30 ± 0.020
1×10^4	0.04 ± 0.005	-0.22 ± 0.010
1×10^2	0.01 ± 0.003	-0.17 ± 0.010
1×10^0	0.01 ± 0.002	-0.02 ± 0.005

**FIGURE 5.22:** Nitrate production of the Zarka at site 5 at different cell concentrations at 25 °C.**FIGURE 5.23:** Nitrite change of the Zarka at site 5 at different cell concentrations at 25 °C.

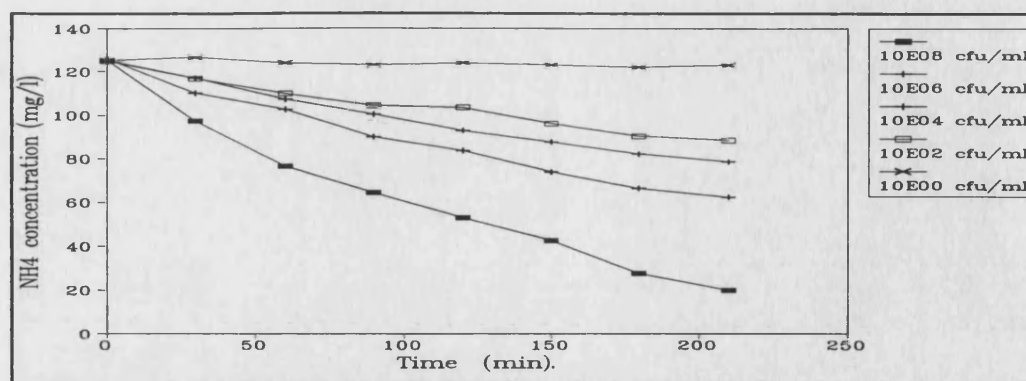


FIGURE 5.24: Ammonium decay of the Zarka at site 5 at different cell concentrations at 25 °C.

The same experiment was also carried out for:

- all other sites with different cell concentrations,
- taking into consideration the effect of chlorination on cell concentration at the treatment plant's outlet (site 2) by taking a sample just before applying chlorination, and another sample after dechlorination by aeration,
- and the change in the physical nature of the river after site 6 where it takes a wider and shallower route.

The same trend at different cell concentrations was observed. However with different rates according to the river conditions at each site. The stoichiometry of the nitrogen compounds was preserved for the different cell concentrations as in the case of the activated sludge. The amount that would appear to be consumed in the production of bacterial cells was higher at higher cell concentrations, i.e. 6% of total available nitrogen, while at the lowest cell concentration experiment it was found to be only 1%.

As mentioned in chapter two, the Qual 2EU model does not take bacteria into consideration, but relates ammonium decay and nitrate production rates to algal biomass. However, the Blackwater model does include bacteria as a main factor in nitrification, but needs to specify the cell concentration of *Nitrosomonas europaea* which is difficult to measure and time consuming. Moreover, the cell concentration has to be given in terms of mg/l rather than a cell count, which is likely to add uncertainty to the cell estimate, because of the difficulty in enumerating *Nitrosomonas europaea* which needs to be isolated before an estimate of the dry cell weight.

Wong-Chong *et al.* (1975) and Prosser (1990) used linear regression analysis to describe the effect of microbial concentration on the oxidation rate. The formula used by these researchers can be described as follows:

$$k_2^* = \frac{k_{2\max}^* k_2 S_{a_m}}{k_{2\max}^* + k_2 S_{a_m}} \quad (5.2)$$

where:

k_2^* is the ammonium oxidation rate, $\text{mgNI}^{-1}\text{h}^{-1}$

$k_{2\max}^*$ is the maximum ammonium oxidation rate, $\text{mgNI}^{-1}\text{h}^{-1}$

k_2 is the reaction rate constant, h^{-1}

S_{a_m} is the bacterial concentration, mg SVS/l .

However, equation (5.2) described by Wong-Chong *et al.* (1975) uses the suspended volatile solids (SVS) as an indicator of the two genera *Nitrosomonas* and *Nitrobacter* concentrations. Adopting the SVS as a biomass indicator assumes that nitrifiers occupy a constant proportion of SVS. Moreover, they derived two separate rate coefficients

for the two types of bacteria involving, k_2 for *Nitrosomonas* and k_3 for *Nitrobacter* (i.e., in addition to providing different rates for ammonium decay and nitrate production, the different cell concentrations should also be provided). Their work was based on a prepared medium of a mixture of urea and casein in a 10:1 ratio, and chicken manure. For the nitrification stages, ammonium and sodium nitrite were used as substrates for ammonium and nitrate experiments, respectively. The culture used was taken from an enriched culture of nitrifying organisms isolated from an oxidation ditch in which nitrification was known to be occurring. It is not clear how k_2 was calculated and this work was not based on a river system.

Reviewing the literature, only one reported piece of work was found which used this type of equation to simulate a river system, (Shima *et al.*, 1978). Two separate equations were derived for the two genera *Nitrosomonas* and *Nitrobacter*. They concluded that their derived model is not intended for direct application to a real river because the experiments were conducted under strictly controlled conditions, but the analysis of the model suggests that nitrification process is an indispensable element for any practical model for real river.

The above mentioned formula will be used in this study to simulate the relationship between cell concentration of total bacterial count, taken as cfu/ml, and rates of nitrate production and ammonium decay. A relationship similar to equation (5.2) was considered as follows and will be referred to as Modified Reciprocal Straight line (MRS):

$$r_1 = \frac{ab[X]}{a+b[X]} \quad (5.3)$$

where:

r_1 is the rate of nitrate production or ammonium decay, mg/l/min.

$[X]$ is the cell concentration, cfu/ml

a and b are relationship constants for either nitrate or ammonium.

The relationship constants were found by using an optimization technique, where by the solution was set to minimize the standard error between measured and calculated rates. These constants were found to be as follows:

$a_N = 0.065 \pm 2.3 \times 10^{-4}$, where a_N relationship constant for nitrate
production

$a_A = -0.308 \pm 2.3 \times 10^{-4}$, where a_A relationship constant for ammonium
decay

$b_N = 1.1 \times 10^{-5} \pm 1.6 \times 10^{-2}$, for nitrate production and

$b_A = -0.004 \pm 1.6 \times 10^{-2}$, for ammonium decay

These findings are shown in figures (5.25a and 5.25b), which show that the MRS model generally succeeded in describing the relationship between cell concentration and nitrate production rate with a standard deviation of 2.3×10^{-4} , but failed with the ammonium decay rate having a standard deviation of 0.016. This could be attributed to the previously mentioned fact that nitrate production is more related to cell concentration, since it involves two types of microorganisms, and also it depends on the reduction of ammonium and nitrite, while ammonium decay is more related to physical properties (e.g aeration, sedimentation, pH, etc..) in addition to microorganisms.

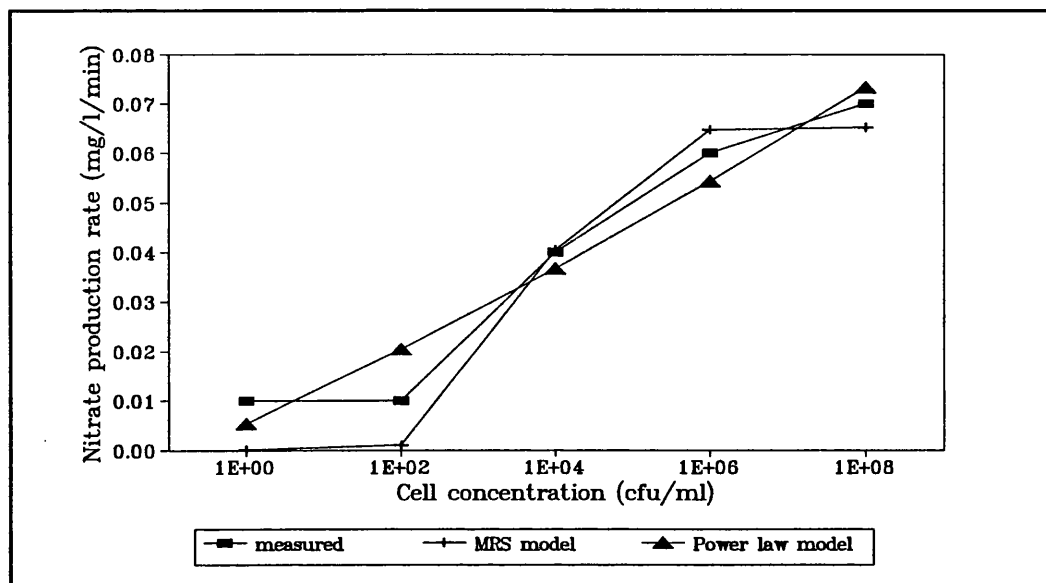


FIGURE 5.25.a: Nitrate production rate of the River Zarka related to cell concentration as measured and modelled by a MRS and a modified power law models.

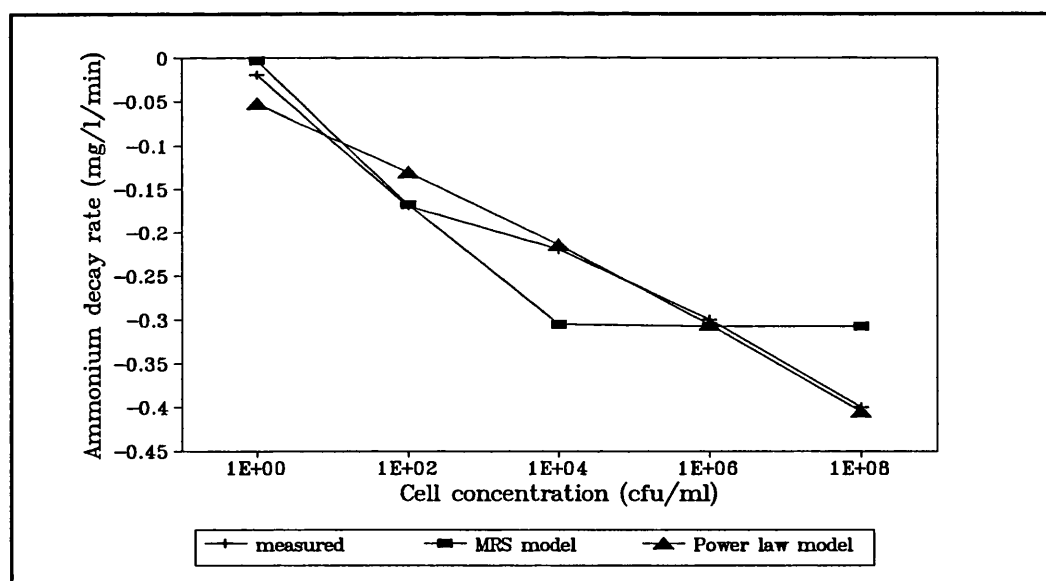


FIGURE 5.25.b: Ammonium decay rate of River Zarka related to cell concentration as measured and modelled by a MRS and a modified power law models.

The relationship between nitrate production and ammonium decay rates and cell concentration was also tested using other types of equations as listed below:

- straight line equation:

$$r_1 = a + b[X] \quad (5.4)$$

- exponential equation

$$r_1 = a + EXP(b[X]) \quad (5.5)$$

- power law equation

$$r_1 = a * [X]^b \quad (5.6)$$

- hyperbola equation

$$r_1 = a + \frac{b}{[X]} \quad (5.7)$$

- reciprocal straight line equation

$$r_1 = \frac{1}{(a + b[X])} \quad (5.8)$$

- reciprocal hyperbola equation

$$r_1 = \frac{[x]}{a + b[X]} \quad (5.9)$$

- polynomial

$$r_1 = a + b[X] + c[X]^2 + d[x]^3 + \dots + n[x]^{n-1} \quad (5.10)$$

where:

r_1 is the rate of ammonium decay or nitrate production, (mg/l/min)

$[X]$ is the cell concentration, cfu/ml

a,b,c,... are relationship constants.

All of these equations failed to describe the relationship between the reaction rates and cell concentration. However, a modified power law was found to give a close relationship, and the equation used can be written as follows:

$$r_1 = a[X]^b + c \quad (5.11)$$

where

$a_N = 0.18$, $b_N = 0.017$, and $c_N = -0.17$ for nitrate production with a

standard deviation of 1.9×10^{-4} and

$a_A = -0.9$, $b_A = 0.018$, and $c_A = 0.84$ for ammonium decay with a standard deviation of 2.7×10^{-3} .

These findings are plotted in figures (5.25a, and 5.25b). However, although equation (5.11) does describe the measured data, it is because they probably fall within the exponential phase of cell growth curve. As can be seen from figure (5.25.a), ammonium decay was better described by the modified power law than nitrate production, because nitrate production is more dependant on cell biomass than ammonium decay, which is more related to physical properties (e.g. reaeration and benthic source or demand). Therefore, the modified power law will only be considered in the case of ammonium decay and the MRS model will be considered in the case of nitrate production. When applying the modified power law, more experiments have to be done at higher cell concentrations to detect the threshold at which any further increase in cell concentration will not lead to an increase in the bacterial activity and hence nitrification rates, then this threshold will be adopted as the system boundary.

As expected, the AS effluent did follow the same trend as the river water using the

MRS model in modelling nitrate production rates and a modified power law model in modelling ammonium decay rates (figures 5.25.c and 5.25.d) in the relationship between cell concentration and nitrification rates. In fact, the MRS model failed to predict ammonium decay rates as related to cell concentration, which suggest that ammonium decay was primarily independent of cell concentration and more related to physical properties (e.g. rate of aeration). However, the MRS model succeeded in the case of nitrate production since this process is more related to the cell concentration and hence microbial activity. Both models can be described for the activated sludge effluent by using the following model coefficients:

- Modelling ammonium using the modified power law, equation (5.11):

$$a_A = -0.038 \quad b_A = 0.102, \text{ and } c_A = -0.002 \text{ with a standard deviation of } 2.7 \times 10^{-3}.$$

-Modelling nitrate production rate using Monod type model, equation (5.3)

$$a_N = 0.388 \quad b_N = 6.8 \times 10^{-5} \quad \text{with a standard deviation of } 4.5 \times 10^{-3}$$

The difference between AS effluent and River Zarka constants may have resulted from the assumption that the biomass is evenly distributed throughout the liquid phase. In activated sludge systems a significant proportion is in the form of flocs introducing substrate diffusion as a factor affecting the rate kinetics (dependent on floc size, diffusion coefficients, and flow patterns). Although, if the throughput time in the activated sludge system is high this would lead to washout of slow growing nitrifiers. This situation for example, would not occur in trickling filter systems because nitrifiers form a component of a multi-species biofilm (Prosser 1990).

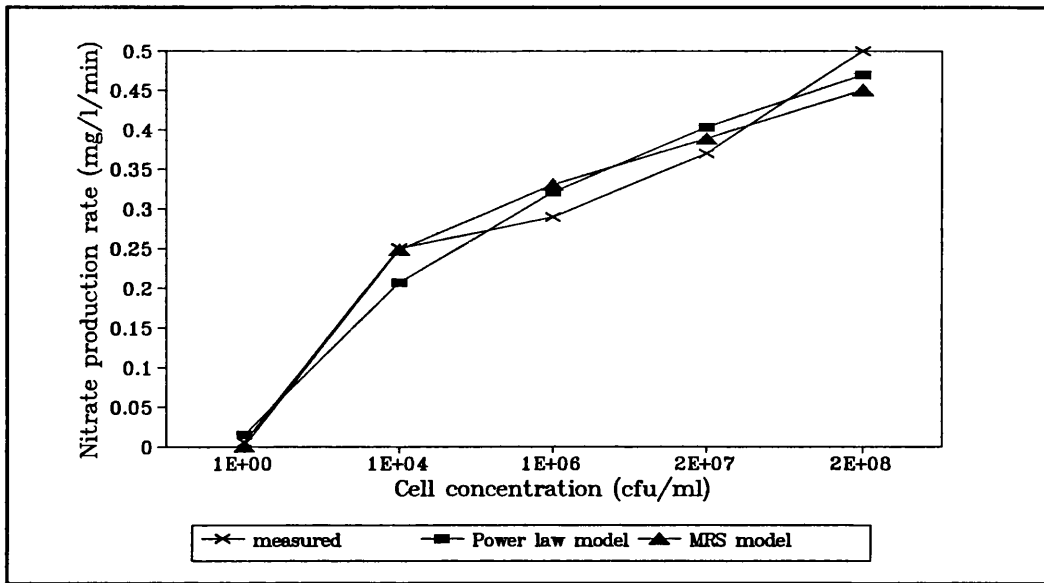


FIGURE 5.25.c: Nitrate production rate of the AS related to cell concentration as measured and modelled by MRS and a modified power law type models.

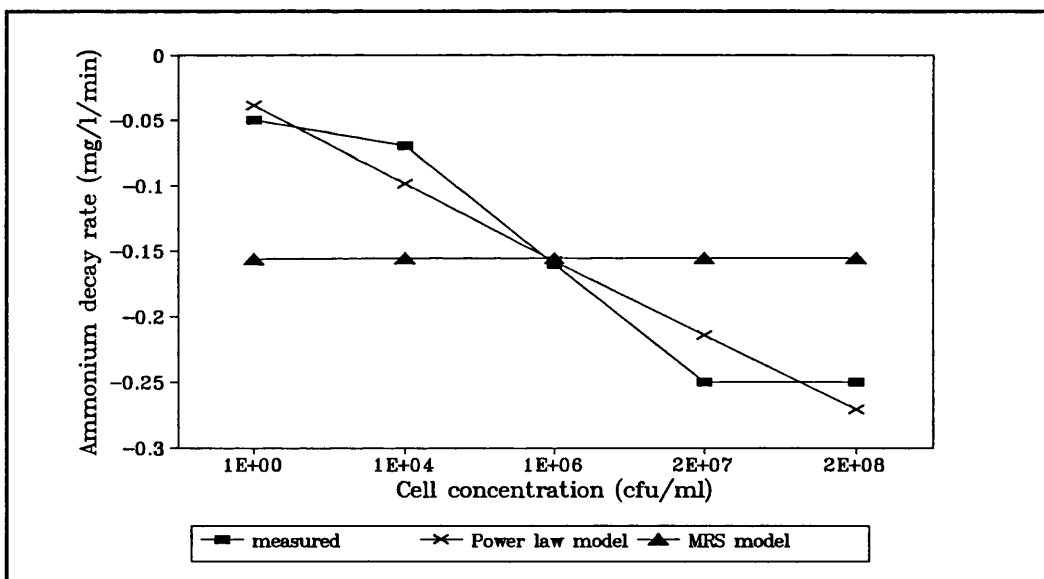


FIGURE 5.25.d: Ammonium decay rate of AS related to cell concentration as measured and modelled by the MRS and a modified power type models.

Furthermore, figures (5.25.c and 5.25.d) suggest that the bacterial activity in the AS started to reach the stationary phase, while in figures (5.25.a and 5.25.b) the bacterial activity in the river water is still within the exponential phase despite the fact that both systems have a similar bacterial count. This can be attributed to the higher capacity of the Zarka water to support higher bacterial activities than the AS system, since the

bacteria in the river water are not adapted to the nitrification process hence it will need more time than in the AS effluent which is probably well adapted to nitrification. This also explains the higher nitrification rates in the AS effluent than in the river water despite that both systems have the same bacterial population.

5.4.3- EFFECT OF LIGHT:

The recorded chlorophyll concentrations in the effluent (site 2) are high (455 µg/l), which suggest a high algal activity (as in the River Seine, France with chlorophyll concentrations of (100-750 µg/l), Garnier *et al.*, 1991). Hence significant response to light intensity variation would be expected. However, from experimentation, the algal activity in terms of oxygen production suggests the opposite. To examine this situation the following experiments were conducted.

Collected river water samples were divided into two sets, one was left subjected to light and the other covered with a black hood to prevent light penetration. Figures (5.26, 5.27, and 5.28) show nitrate, nitrite and ammonium concentrations under light and dark conditions. These figures show that nitrification was not affected by the absence of light, and suggests that algal activity over the experimental period was insignificant. The resulting rates for both light and dark experiments were the same and are given in table (5.6). Sites 2, 5, and 6 were selected to represent the wastewater treatment plant's outlet, the river before mixing with the tributary, and the river after mixing, respectively.

TABLE 5.6: Nitrification rates at selected sites along the river under light and dark.

Rate (mg/l/min)		Site 2	Site 5	Site 6
NO ₃ production	Light	0.04 ± 0.003	0.04 ± 0.004	0.06 ± 0.008
	Dark	0.04 ± 0.002	0.04 ± 0.004	0.055 ± 0.010
NH ₄ decay	Light	-0.29 ± 0.010	-0.37 ± 0.020	-0.28 ± 0.010
	Dark	-0.29 ± 0.005	-0.37 ± 0.020	-0.23 ± 0.008

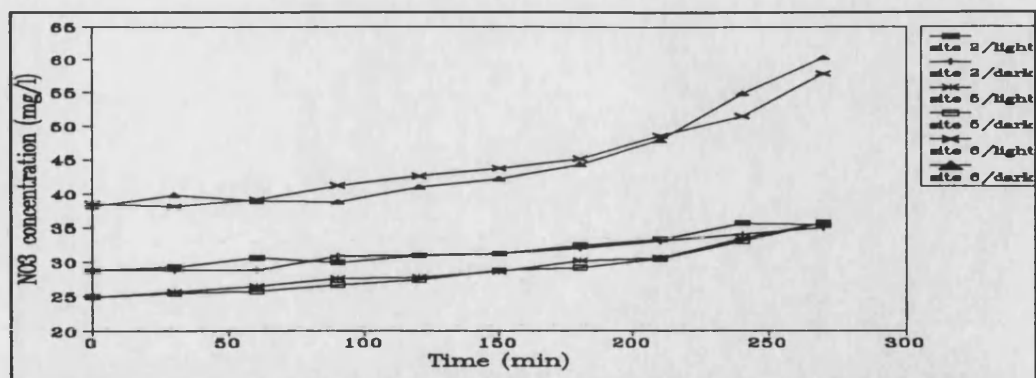


FIGURE 5.26: Nitrate production under light and in the dark at different sites at 25 °C.

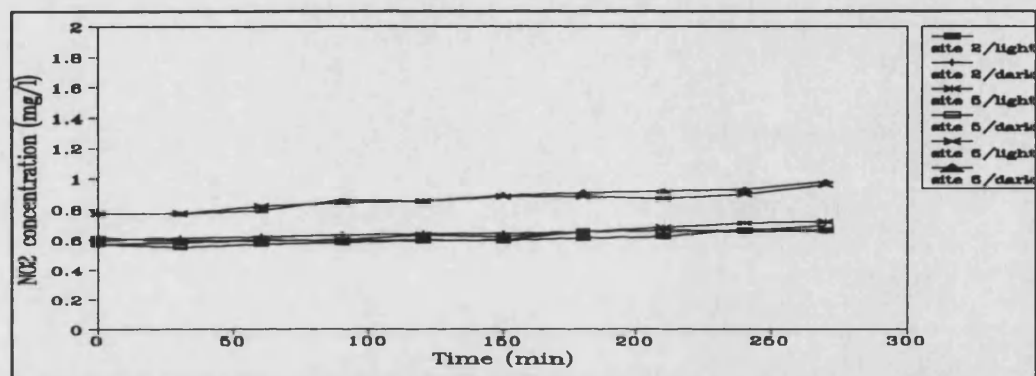


FIGURE 5.27: Nitrite change under light and in the dark at different sites at 25°C.

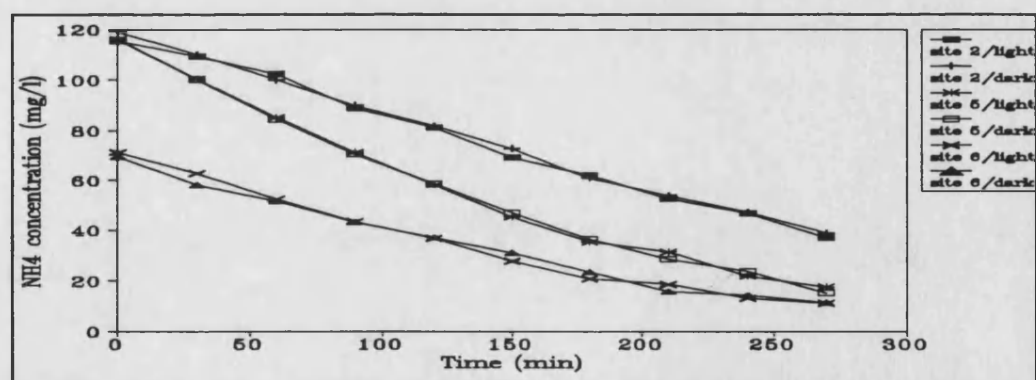


FIGURE 5.28: Ammonium decay under light and in the dark at different sites at 25 °C.

Figure (5.29) shows deoxygenation (after cutting off the oxygen supply) at the same sites and under the same conditions of temperature and cell concentration. It shows that deoxygenation was affected by the absence of light at the down-stream sites more

than at the up-stream sites, (site 5 had to be oxygenated before measuring DO reduction since the initial amount of DO was too low to be indicative). Again, this was unexpected in terms of chlorophyll concentration as at up-stream sites ($455 \mu\text{g/l}$) it is higher than that at the down-stream sites ($130 \mu\text{g/l}$). This indicates that chlorination at site 2 (the wastewater treatment plant effluent) which is used to kill bacteria also has inhibited algal activity. However, the difference in the deoxygenation rates between light and dark samples at the down-stream sites is still small (table 5.7), which indicates that the algal activity remains low even after the free chlorine reduces.

TABLE 5.7: Deoxygenation rate along the river under light and dark.

Deoxygenation rate (mg/l/min)	Site 2	Site 5	Site 6
Light	$-0.004 \pm 8 \times 10^{-4}$	-0.07 ± 0.003	-0.02 ± 0.002
Dark	$-0.005 \pm 9 \times 10^{-4}$	-0.09 ± 0.001	-0.04 ± 0.002

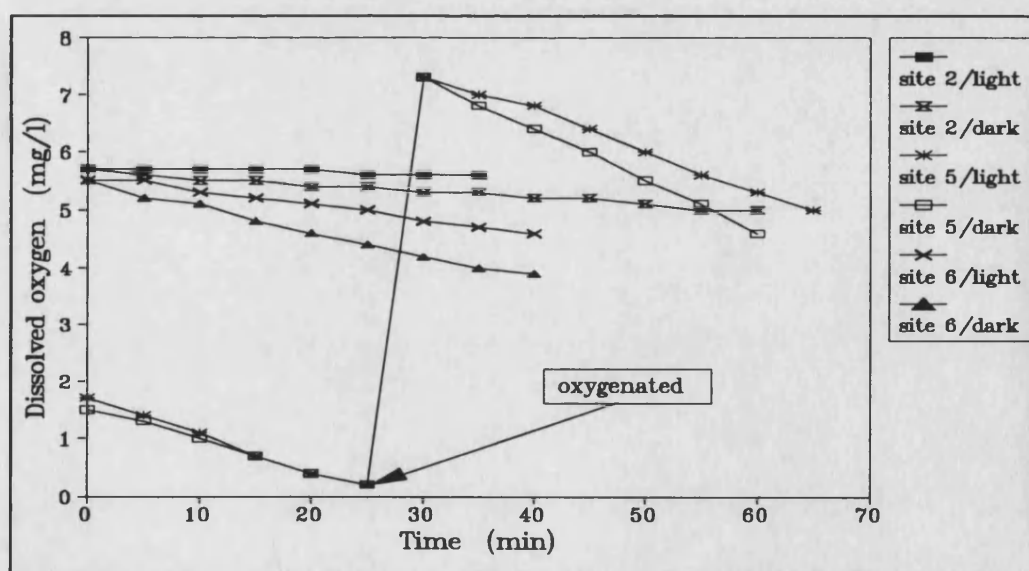


FIGURE 5.29: In-situ deoxygenation at different sites under light or dark.

The incident solar radiation varies with time and position, and is the energy source for photosynthetic growth. In a natural river environment the light intensity is not uniformly at the optimum value, but varies as a function of depth due to turbidity

present (self shading) and the time of day. Thus in lower layers, intensities are generally below the optimum and at the surface may be above the optimum, so growth rates would be inhibited. If the water system is deep enough, i.e. lakes and sizable rivers, there would be a third intermediate layer which would facilitate the production of chlorophyll, as high light intensities are reduced when passing through the surface layer.

Barber (1987) reported that decrease in photosynthetic rate is rapid under high light intensities "photoinhibition" (of the order of a few minutes to an hour), but recovers at a slower rate when returned to low light. The loss in activity due to photoinhibition occurs without a significant reduction in the amount of bulk chlorophyll.

The high chlorophyll concentration of the river is misleading as it is generally considered that a high concentration represents high algal activity, reflected by oxygen production in the light. The experiments carried out on the Zarka do not show this as deoxygenation rates in both cases were more or less the same. This means that inspite of a high chlorophyll concentration, algal activity is low, which means that algae are being inhibited before being discharged into the river, either by chlorination and water toxicity, or by photoinhibition due to high solar radiation intensities in that area. Algae may lose sensitivity to photoinhibition when adapted to higher light intensities. The adjustment can be quite rapid, i.e. less than a generation time (Lewis *et al.*, 1984 as cited by Barber, 1987).

The depth in the plant lagoons (2-5 m) is much greater than in the river (0.3-0.6 m),

i.e. the whole water column of the river is subjected to high solar radiation intensities, while in the lagoons, there are probably three layers, the middle of which is likely to be subjected to optimum light intensity, allowing algae to be produced, while the surface layer is subjected to high light intensities which could inhibit algal production, and the bottom layer is subjected to self-shading which minimizes the algal production.

Nixon and Berounsky (1984) found that photoinhibition was detected as a nitrification inhibitor in the River Providence/U.S.A.. They also found that some sort of toxicity in the river water inhibited complete nitrification and resulted in low nitrification rates, although they did not identify the type of toxicity. However, unfortunately the method of N^{15} tracing used in their study makes it difficult to compare their rates with the Zarka.

5.4.4- DIURNAL TEMPERATURE AND OXYGEN VARIATION:

The difference between the highest and the lowest water temperature of the day was 10°C. This high difference is rarely found in other river systems and is symptomatic of a very shallow river which is responsive to atmospheric changes.

Recorded diurnal oxygen and temperature variations are represented in figures (5.30 and 5.31). It is clear that oxygen responds to the time of the day in the down-stream sites more than in the upstream sites. In part this can be attributed to higher photosynthetic activity down-stream, which can be related to lower velocities (0.5 m/s before site 6 and 0.3 m/s after site 6). Below site 6, where the river is wider and shallower, sedimentation of algae and the possibility of growth are higher, (i.e., higher

velocities flush away algae and prevent growth). However, and despite high chlorophyll concentrations in the river, the algal activity was very low and does not appear to correspond directly to chlorophyll concentration.

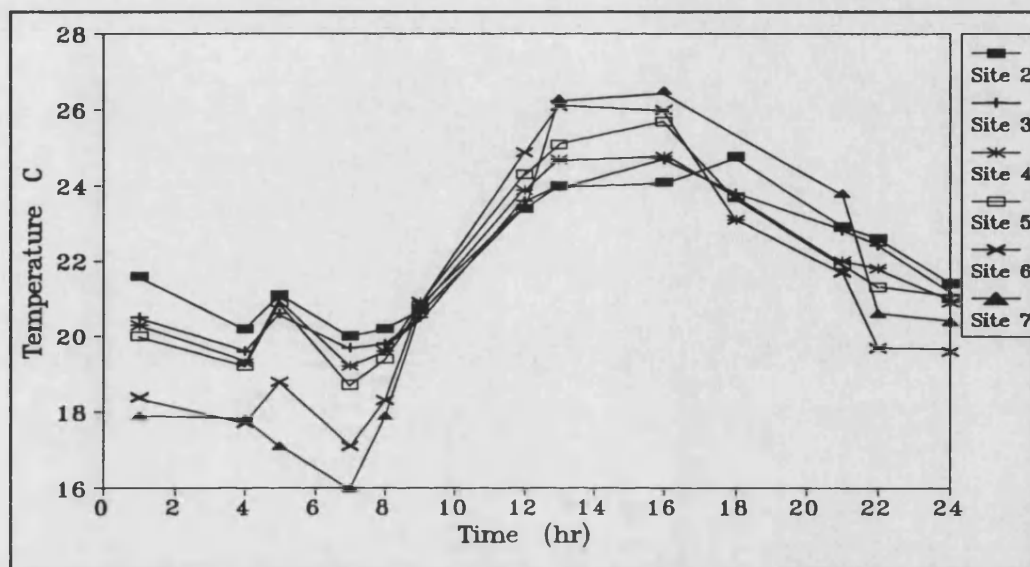


FIGURE 5.30: Diurnal temperature variation at selected sites of River Zarka.

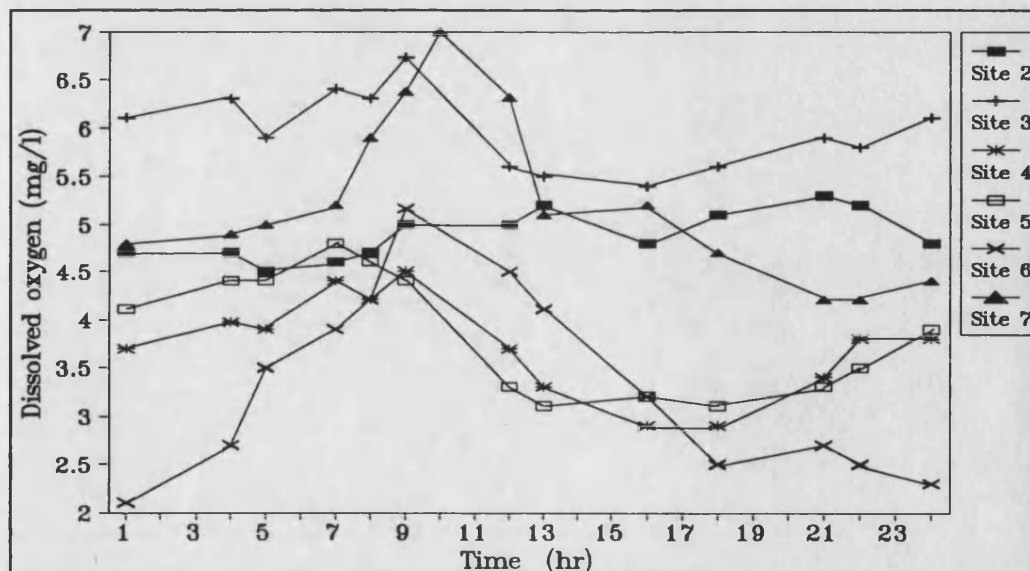


FIGURE 5.31: Diurnal dissolved oxygen variation at selected sites of the River Zarka.

Figure (5.32) shows that while chlorophyll concentrations decrease, algal or photosynthetic activity appears to increase when represented by the difference between maximum and minimum diurnal dissolved oxygen concentrations. Generally, this would not be the case, as an increase in algal activity should be accompanied by an increase in chlorophyll concentration, i.e. high chlorophyll concentrations represent high algal biomass, which means more oxygen production during day light and more respiration over the whole day.

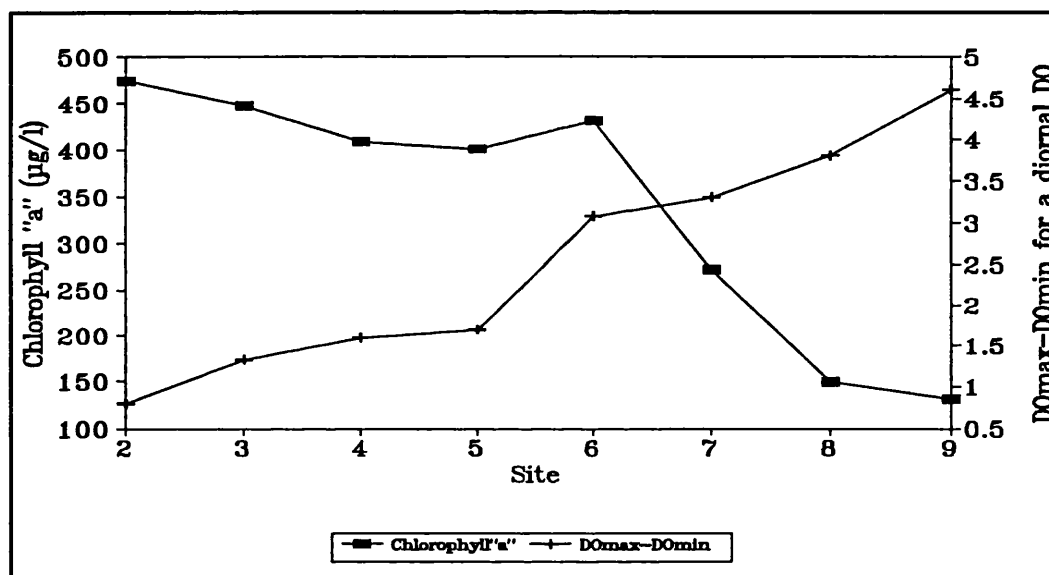


FIGURE 5.32: Chlorophyll "a" versus algal activity represented by the difference between minimum and maximum diurnal DO along the river.

It is concluded that much of the algal biomass present in the river was either not viable, or its activity was severely affected. Algae were produced in the stabilization ponds of the treatment plant, but were deactivated by chlorination or photoinhibition. Photoinhibition may occur when algae were suddenly exposed to high light intensities after being discharged from the lagoons, as the effluent at site 2. This can be demonstrated by comparing diurnal DO of the river (at site 5 before, and site 6, after mixing with the tributary) with that of the tributary which contains ten times less

chlorophyll than the Zarka's water, but exhibits higher photosynthetic activity (figure 5.33).

However, algae start to re-establish down-stream of site 5 which explains the higher photosynthetic activities. The lower chlorophyll content of the tributary (and that locally produced along the river) associated with high oxygen production, is a result of algae that can tolerate high light intensities.

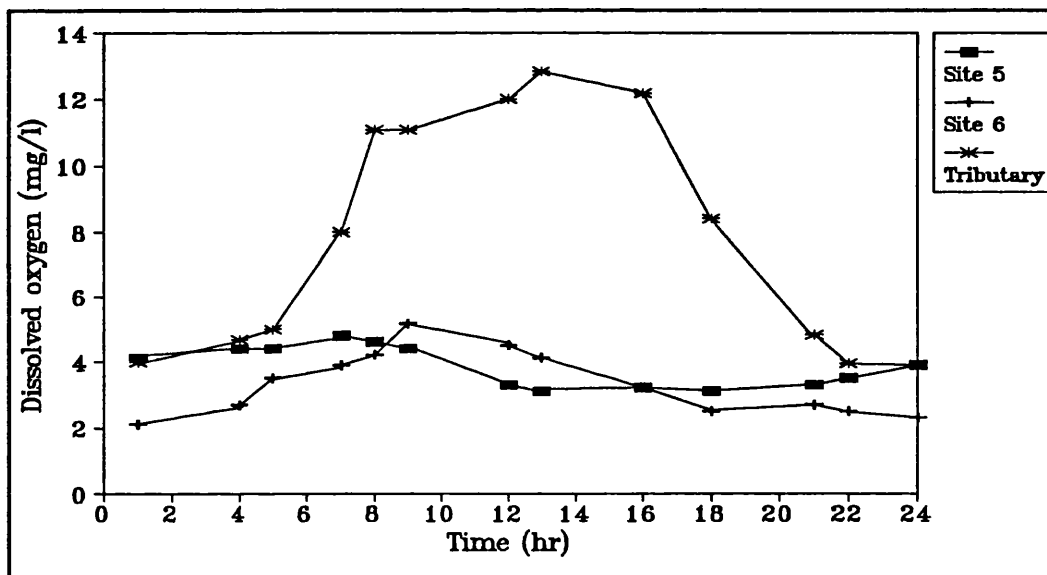


FIGURE 5.33: Diurnal dissolved oxygen of the tributary compared to the Zarka before and after confluence.

5.4.5- EFFECT OF RIVER BED SEDIMENT:

The sedimentation rate (in terms of the TSS) and the velocity of a river are important physical parameters in affecting the water quality of the river. The worst combination of these parameters occurs during summer low flow, i.e., the velocity is the lowest and the sedimentation rate is the highest. However (every year) during winter the Zarka is subjected to several floods resulting in scouring of sediments deposited during the preceding summer. This adds a further complication to modelling the effect of the

sediment on the river. The following experiments were carried out during low flow at the beginning of summer when sedimentation took place.

Water samples from the different sites were collected and divided into two sets. The first set was placed under light and the second was placed in the dark. Each of these sets was sub-divided, the first left without adding sediment, while to the second set, between 250-500 g \pm 1g of river bed sediment from the relevant river site was added (the quantity dependent on how much was removed from bed area of 0.071 m² at each site, that is the cross-sectional area of the 15cm diameter columns). The height of the sediment ranged between 3-5cm and the height of the water column in the container above the sediment 30-60cm (450-900ml), both of which represent the actual depths found at the river sites.

Figure (5.34) shows the weight of the sediment measured and used in the above experiments along the river. It is clear that sedimentation increases down stream as a consequence of decreasing velocity.

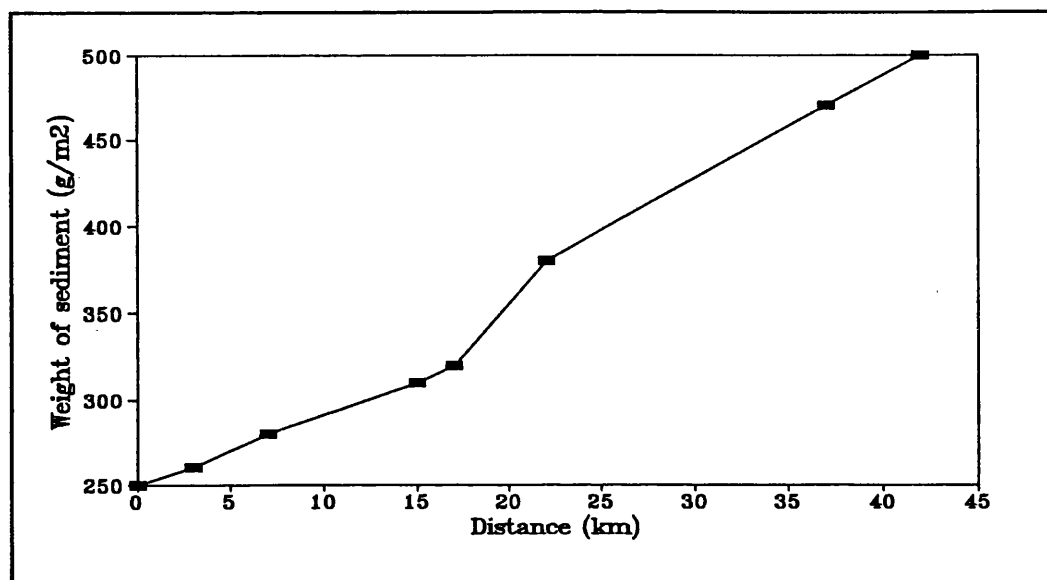


FIGURE 5.34: Weight of sediment at each site along the river.

It can be seen from figures (5.35, 5.36, and 5.37), that samples containing river sediment (placed under light), exerted lower nitrification rates than samples without sediment. The rate of ammonium decay as shown in figure (5.37) and table (5.8), decreased after site 5, and this could be attributed to lower river velocities and shallower waters at down-stream sites in addition to lower bacterial concentrations. Although, the sample containers did not allow for a direct representation of velocity change, the type of sediment did indirectly represent the result of velocity effects. That is, at lower velocities, algae and other detritus bacteria tend to settle, therefore, the amount of sediment will be higher and accordingly the oxygen demand will be higher due to organic degradation. Consequently, despite the higher photosynthetic activity, the production of oxygen is not enough, and oxidation of ammonium is less down-stream where more sediment oxygen demand is needed, which cannot be substituted by the oxygen photosynthetically produced.

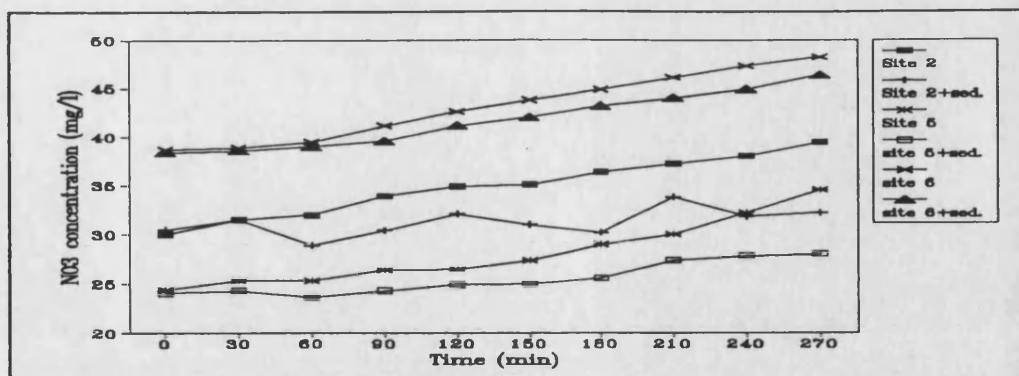


FIGURE 5.35: Nitrate production at selected sites along the river in the presence of light and with or without river sediment.

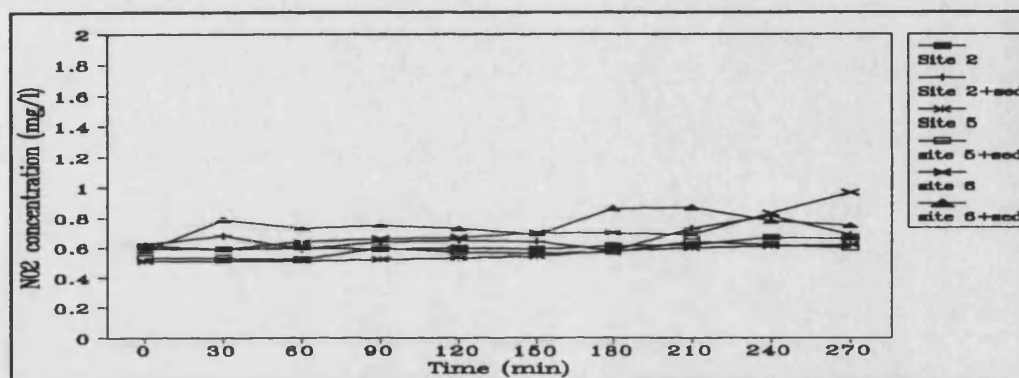


FIGURE 5.36: Nitrite change at selected sites along the river in the presence of light and with or without river sediment.

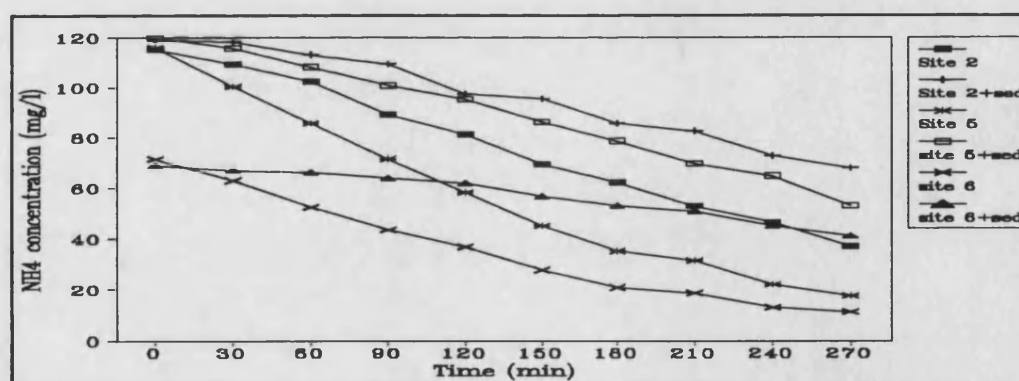


FIGURE 5.37: Ammonium decay at selected sites along the river in the presence of light and with or without river sediment.

In another experiment, site 8 was chosen to represent the natural purification capacity of the river after being naturally well aerated and a significant amount of sediment and algae had built-up. A water column from this site was prepared (in the same way as

previously) to measure deoxygenation with and without the presence of sediment, as well as under light and dark (after cutting off the oxygen supply). Figure (5.38) shows that the presence of sediment exerted higher oxygen demand and resulted in a faster deoxygenation rate ($0.02 \pm 7 \times 10^{-4}$ mg/l/min with sediment and $0.01 \pm 3 \times 10^{-4}$ mg/l/min without sediment). It is also clear that the oxygen demand due to the sediment is higher than that just due to light cut-off (0.015 ± 0.001 mg/l/min in the dark without sediment). This could be attributed to higher oxygen consumption of settling bacteria and algae which could not be fully substituted by production of oxygen due to photosynthesis in the presence of light since algal activity is too low. The water contains high levels of biomass of both algae and bacteria which would settle and therefore increase the sediment oxygen demand due to their respiration (if viable) and subsequent degradation.

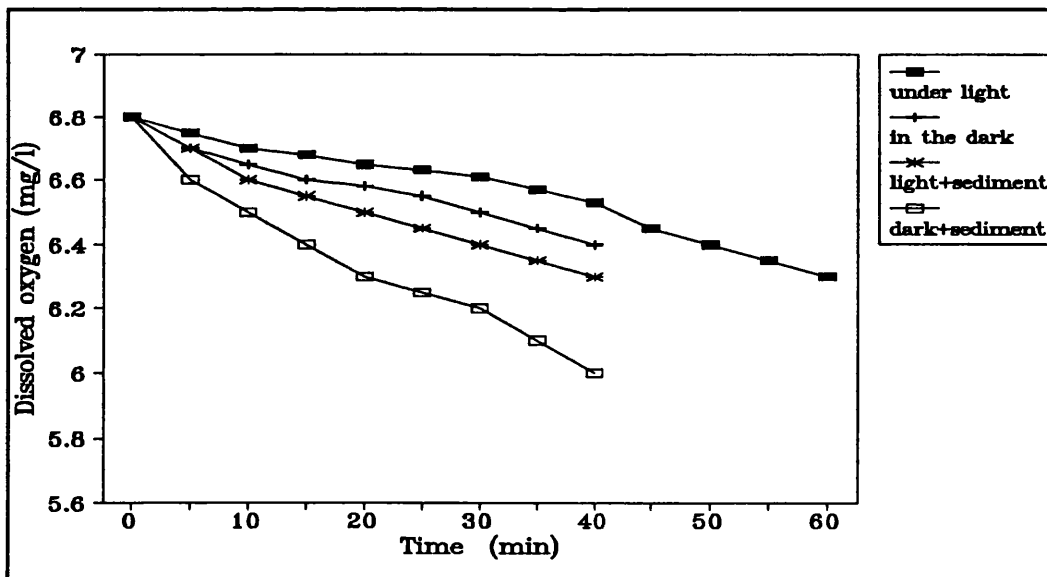


FIGURE 5.38: Deoxygenation of river water under light and dark and in the presence and absence of river bed sediment at site 8.

TABLE 5.8: Nitrification rates in the presence and absence of river bed sediment along the river under light and dark.

Rate	incubation	Site 2	Site 5	Site 6
NO ₃ production rate (r_2) (mg/l/min)	Light	0.04 ± 0.003	0.04 ± 0.004	0.06 ± 0.008
	Light with sediment	0.03 ± 0.004	0.02 ± 0.002	0.04 ± 0.002
	Dark	0.04 ± 0.002	0.04 ± 0.004	0.055 ± 0.010
	Dark with sediment	0.03 ± 0.004	0.016 ± 0.002	0.03 ± 0.004
NH ₄ decay rate (r_1) (mg/l/min)	Light	-0.29 ± 0.010	-0.37 ± 0.020	-0.28 ± 0.010
	Light with sediment	-0.22 ± 0.010	-0.29 ± 0.006	-0.13 ± 0.007
	Dark	-0.29 ± 0.005	-0.37 ± 0.020	-0.23 ± 0.008
	Dark with sediment	-0.20 ± 0.010	-0.25 ± 0.006	-0.09 ± 0.008

This agrees with the previous findings, that oxygen provided by photosynthesis cannot fully compensate for oxygen consumed by sediment. This is true for all sites along the river, the only difference is in the amount of sediment oxygen demand and photosynthetic activity, which is relative to an extent to the amount and rate of sedimentation.

Nitrification was insignificantly suppressed when samples with sediments were placed in the dark, (figures 5.39, 5.40, and 5.41). The degree of the effect of light (as a source of oxygen due to photosynthesis), increased moving down-stream as a consequence of increased photosynthetic activity. Hence cutting off light reduces the availability of oxygen which increases observed oxygen depletion rate.

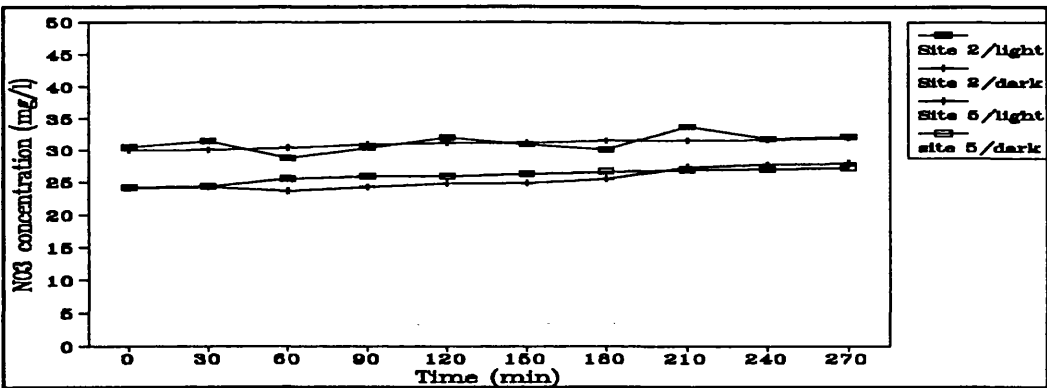


FIGURE 5.39: Change in nitrate at selected sites along the river placed in light or dark with river sediment.

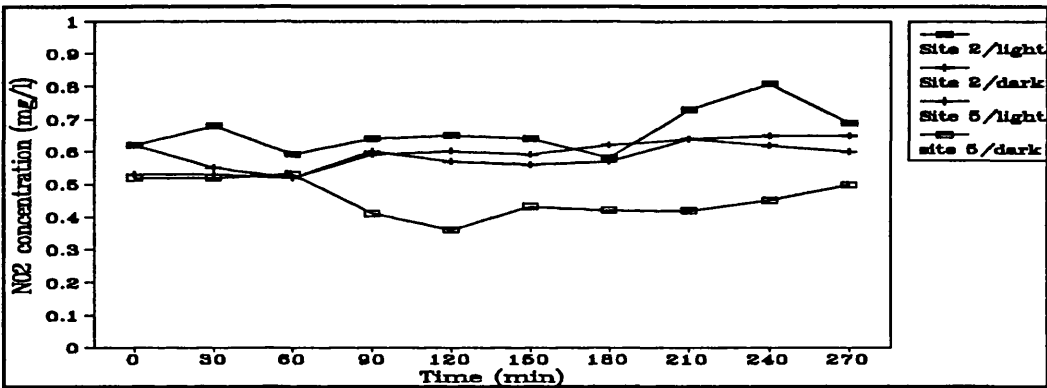


FIGURE 5.40: Change in nitrite at selected sites along the river placed in light or dark with river sediment.

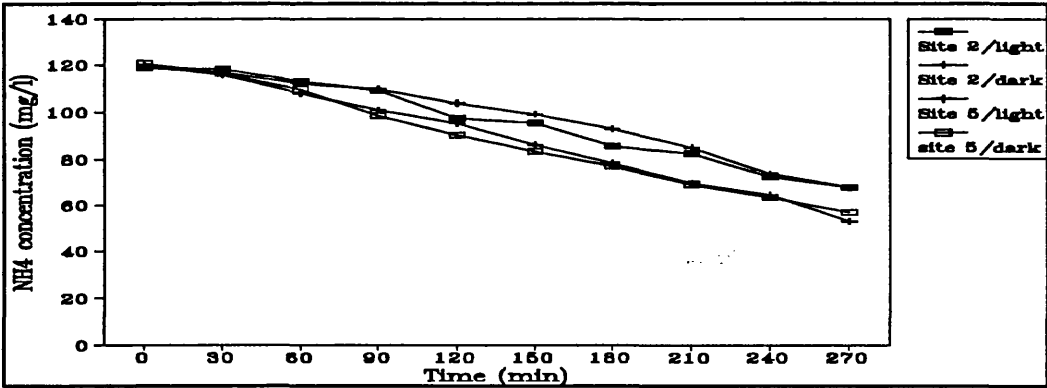


FIGURE 5.41: Ammonium decay at selected sites along the river placed in light or dark with river sediment.

5.4.6- EFFECT OF AERATION AND OXYGEN CONCENTRATION:

This experiment (represented here by site 6 but carried out for all the different sites) showed that the decay rate of ammonium was highly dependent on the concentration

of oxygen. Previous work reported by Arceivala (1981) has indicated that oxygen should be provided in sufficient amounts (3-4 mg/l) in a river system for nitrification to take place (for both ammonium decay and nitrate production), even if all other conditions are favourable. Eckenfelder (1989) reported that oxygen should be in excess of 2 mg/l for nitrification to occur but he did not specify which stage of nitrification, i.e. ammonium decay or nitrate production. In this study, both rates were considered separately in order to find separate oxygen concentration ranges for the stages of nitrification to take place.

As the concentration of provided oxygen was increased in the samples, ammonium decay rate also increased. A minimum concentration of oxygen of 3-4 mg/l was needed for a noticeable reduction (a rate of 0.08 ± 0.003 mg/l/min). However, at a level of 7 mg/l of oxygen, the rate was 5-6 times faster with a rate of 0.22 ± 0.01 mg/l/min. While nitrate production and the change in nitrite showed a response only at the higher oxygen concentration (7 mg/l) with a nitrate production rate of 0.06 ± 0.003 mg/l/min, (figures 5.42, 5.43, and 5.44). This indicates a significant difference between this and other reported work and literature when one oxygen range was typically adopted for both ammonium decay and nitrate production. Separate rates will result in more accurate modelling.

The oxygen level for the ammonium decay found here agrees with literature values because ammonium is a labile substance and tends to decay naturally, while nitrate production is more complicated involving two types of microorganism and needs favourable conditions.

This indicates the toxic nature of the river probably due to the presence of heavy metals such like boron (see section 4.1) due to incomplete treatment at the wastewater treatment plant (the main continuous source of the river), and indeed the high oxygen demand, where high oxygen concentrations are needed to promote nitrification, in spite of the fact that the river contains a high bacterial population.

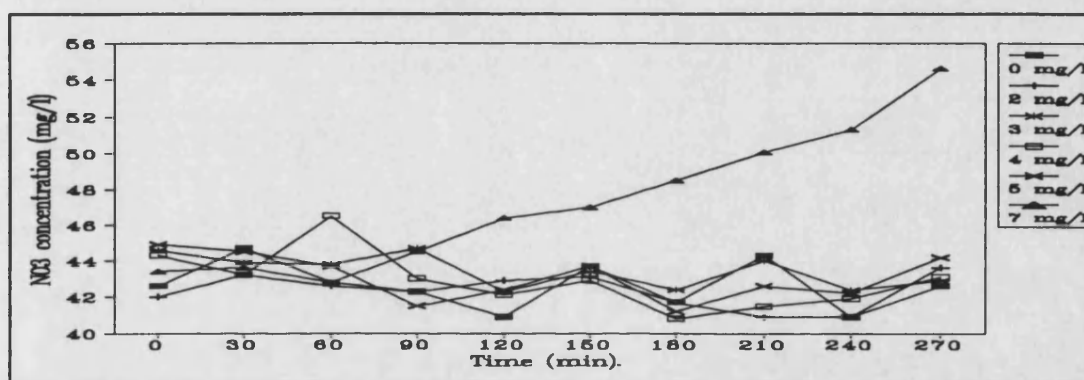


FIGURE 5.42: Change in nitrate at site 6 aerated with different oxygen concentrations at 25°C.

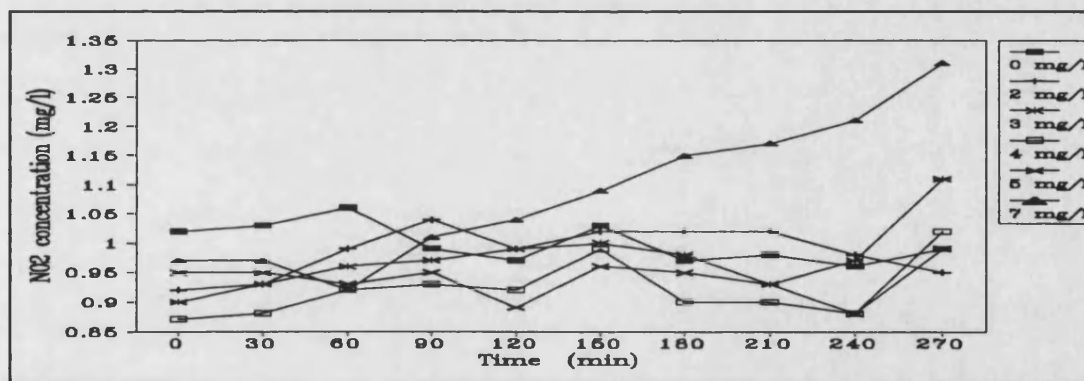


FIGURE 5.43: Change in nitrite at site 6 aerated with different oxygen concentrations at 25°C.

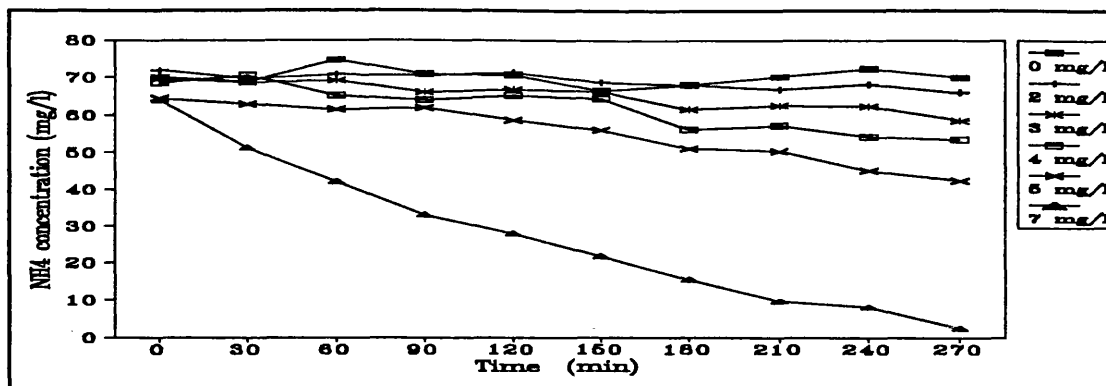


FIGURE 5.44: Ammonium decay at site 6 aerated with different oxygen concentrations at 25°C.

5.4.7- TOTAL SUSPENDED SOLIDS:

The total suspended solids (TSS) content of the river water was followed along the river course and the average of five runs is plotted in figure (5.45). This figure illustrates the decrease in TSS concentration in accordance with bacterial decay, the decrease in the river velocity, and the shallower path that it takes. However, TSS concentration increased at sites two and three due to local turbulence from higher velocities. The overall rate of settling of suspended solids was calculated to be 0.01 ± 0.001 g/l/km.

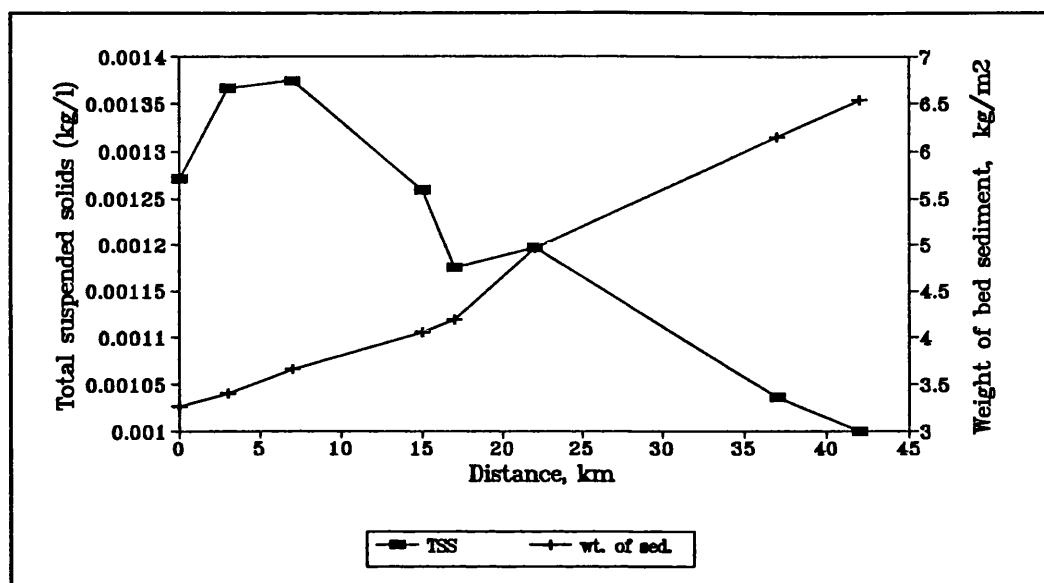


FIGURE 5.45: Suspended solids concentration along the river (average of 5 runs at off-flood periods) related to weight of sediment.

5.5- SUMMARY AND CONCLUSIONS:

A review of literature on nitrification rates showed large discrepancies between reported values for different water systems. Table (5.9) shows nitrification rates as ammonium decay rates for different water systems, including the present work on the River Zarka and the activated sludge effluent. Most researchers prefer to express nitrification rate in terms of ammonium decay since nitrate production is more complicated as it involves two stages and more than one type of microorganism. Differences in the rates reported in table (5.9) are due to the different nature and conditions surrounding the systems, and also the experimental method used can be a substantial factor in affecting the results.

TABLE (5.9): Nitrification rate of different water systems at 20 °C.

Water System	Reference	Nitrification * Rate (mg/l/min)
Willamette	Hines et al. (1978)	0.30
Ostanaula	Cooper (1986)	4.64
Trace	Cooper (1986)	4.82
Kanawha	Tze-Wen et al. (1980)	2.5×10^{-6}
South Chickamauga	Cooper (1986)	0.08
Mine	Cooper (1986)	20.54
Orona	Cooper (1986)	2.95-16.97
Waiohapu	Cooper (1986)	1.07-7.14
Waiohewa	Cooper (1986)	8.20-16.61
Winooskey	Benschoten et al. (1984)	2.1×10^{-4} - 1.4×10^{-3}
Sludge in a batch reactor	Wild (1970)	0.536
White	Kennedy (1986)	6×10^{-5}
Toujiang	Yongming (1988)	1.3×10^{-4}
Boise	Chen et al. (1975)	4.2×10^{-5}
Activated sludge effluent	Present study	0.14
Zarka River (site 2)	Present study	0.29
(site 5)		0.40
(site 6)		0.15

* Taken as the decay rate of ammonium.

However, the kinetics of biological nitrification are not yet thoroughly understood and a number of different rate equations have been derived. Each of these rate equations leads to a different set of design parameters and stems from different original assumption, and therefore, not surprisingly different results have been produced. They also emphasize the importance of taking local measurements to obtain good

representation of the system under study.

Rates of biochemical oxidation of ammonia and nitrate are naturally unstable, and large sampling errors are unavoidable. Many factors determine the rate and extent of nitrogenous oxidation. For example, on sunny days (if there are no other factors affecting the activity of algae) most of the ammonia present in the stream may be absorbed directly in the metabolic processes of algae, slowing or halting the production of nitrites and nitrates. Variations in rates of nitrogenous oxidation from this source and from many other causes make it difficult to select appropriate input parameters for computer models that attempt to simulate the natural processes of river self purification.

The variation in nitrification and denitrification rates in this table and in the different papers can be due to:

- the different types of hydrogen donating material (endogenous or exogenous);
- the suspended solids parameter used to estimate the hydrogen donors and the active mass of organisms;
- different time intervals used in computing the rates;
- different type of rates whether being an initial or an overall rates;
- different physical and chemical characteristics of the studied system;
- different experimental procedures.

Moreover, most of the previous studies have assumed *a priori* the order of the decay. The decision on reaction order has important consequences when the model is used for predictive purposes.

Therefore, it is concluded that different assumptions, experimental procedures and data interpretation will lead to the different conclusions. More explicit studies are necessary to examine the rate equations of nitrification particularly for rivers, such as the Zarka, which are shallow, polluted and flow through semi-arid regions.

Providing different oxygen concentrations to the activated sludge effluent samples, seeded with Zarka concentrations of nitrogenous compounds, showed that the minimum oxygen concentration necessary for both ammonium decay and nitrate production was between 3-4 mg/l of oxygen. While the Zarka water also needed a minimum concentration of 3-4 mg/l of oxygen for a noticeable ammonium decay, but around 7 mg/l for nitrate production. This indicates that in spite of a high cell concentration in the River Zarka, the toxicity of the water (and not the substrate concentration), inhibited nitrification by increasing the oxygen demand and decreasing the photosynthetic activity. The water toxicity is most probably due, at least in part, to high boron concentrations (3.0 mg/l) which have been proved to be toxic to plants in the surrounding agricultural area (section 4.1). Other heavy metals (copper and chromium) originating from nearby industries are also likely to cause problems. This toxicity should be thoroughly investigated in any future development on the Zarka. However, above the minimum level of required oxygen, both systems (the AS effluent and the River Zarka) were affected by the amount of oxygen provided.

Table (5.10) illustrates nitrate production and ammonium decay rates of both the activated sludge effluent and the Zarka water at different oxygen concentrations. The rate of nitrate production when oxygen was not limited for the AS effluent was 3-4 times greater than that for the Zarka water. While for ammonia oxidation it was similar.

This indicates that the first nitrification stage is not rate limiting, hence nitrification should be considered as two stage process rather than a one stage process. The production of nitrate in the second stage of the process is more complicated, since it depends on the decay of ammonium and involves two types of bacteria (*Nitrosomonas europaea* and *Nitrobacter winogradskyi*), the second of which is slower than the first and depends on the presence of *Nitrosomonas europaea*. Probably the toxicity of the river water resulted in lower rates for the production of nitrate, which might explain the difference between nitrate production rates of the AS effluent and the Zarka water.

TABLE 5.10: Nitrification rates of activated sludge effluent and the Zarka water at different oxygen concentrations.

	Rate of AS effluent (mg/l/min)				Rate of River Zarka water (mg/l/min)			
O ₂ conc. mg/l (±0.20)	0	2	4	7	0	2	4	7
NO ₃ production	0.03	0.08	0.18	0.20	0.002	0.006	0.01	0.06
NH ₄ decay	-0.02	-0.06	-0.10	-0.13	-0.002	-0.01	-0.06	-0.15

At different temperatures, both systems showed the same trends, albeit with different rates, hence the effect of temperature on nitrification is not significantly affected by

the quality of the water. Also, changing cell concentration in both systems had a similar effect on the nitrification trend, although actual rates were different.

The power law was found to provide good correlation between temperature and nitrification rates. A modified power law was found to best describe the relationship between cell concentration and ammonium decay rate. The MRS (Modified Reciprocal Straight line) model succeeded in simulating nitrate production, but failed to adequately simulate ammonium decay since the latter depends on physical factors such as natural purification through aeration in addition to its dependence on microbial cells.

The chlorophyll content of the Zarka water does not directly represent the actual algal activity of the river due to chlorination at the treatment plant outlet, toxicity of the water, and photoinhibition due to high solar radiation intensities. The photosynthetic activity measured in the river, probably represents only algae freshly produced along the course, and for a true representation of activity, another type of indication rather than the difference between the minimum and maximum oxygen concentrations in a diurnal DO may be preferable. The sediment oxygen demand is higher downstream in response to lower down-stream velocities and increased sedimentation. Oxygen consumption due to sediment oxygen demand cannot be totally substituted by oxygen produced due to algal activity, such that any increase in oxygen concentration along the river, is attributed to improved surface reaeration.

CHAPTER SIX

APPLICATION OF TWO RIVER WATER QUALITY MODELS TO RIVER ZARKA

6.1- INTRODUCTION:

Prior to any modelling attempt of a water system, available models should be tested for applicability to the system in concern. The problem must be thoroughly investigated and points of concordance or disagreement pointed out to save time and effort in modelling a system that can be described by other models. When other models partially fail to describe the system of interest, modification is necessary to account for points of disagreement, while when they completely fail in simulating the system, a new model has to be designed.

The Zarka river system is characterized by its high bacterial and algal content along with a high level of nitrogen compounds, therefore a model that considers all these parameters is probably required. Unfortunately, no such model was found in the literature. It was found that nitrification models were either controlled by bacterial biomass (Casapieri *et al.*, 1978), or by algal biomass (Van-Benchoten *et al.*, 1984), but not both. Accordingly, a decision was made to consider well known models which consider one of these two main factors, the Blackwater and Qual 2EU models described in sections (2.4.1 and 2.4.2). Nitrification in the Blackwater model is controlled by the concentration of bacteria, while in the Qual 2EU, nitrification is controlled by algal concentration.

The results described in this chapter emphasize the unusual and special nature of this river, as for most of the year, the prime source is the outfall from large stabilization

ponds. The major components studied were ammonium-N, nitrate-N, dissolved oxygen and biochemical oxygen demand. The simulations of both models revealed the necessity of having special assumptions, coefficients and rates, and more profoundly a special model that describes the Zarka and similar water systems.

Furthermore, the short residence time relative to the high initial inputs of ammonia-N and low dissolved oxygen concentrations of the river, hindered self purification. There was also an unusual relationship between algal biomass and activity.

6.2- DESCRIPTION:

Before starting implementation of the two models, general information about the Blackwater river and the Winooski river catchments must be mentioned to highlight differences between both systems and the River Zarka.

Casapieri *et al.* (1978) described and simulated the River Blackwater by the Blackwater model and Van-Benchoten *et al.*, (1984) described and simulated the River Winooski by the Qual 2EU model. Table (6.1) illustrates the differences between these two river systems and the River Zarka. The equations describing the Blackwater model are discussed in section 2.4.2 and illustrated in equations (2.16 through 2.32), while those describing the Qual 2EU model are discussed in section (2.4.1) and illustrated in equations (2.10 through 2.15).

TABLE 6.1: Difference in conditions of the Blackwater, Winooski, and Zarka rivers.

Parameter	River Blackwater	River Winooski	River Zarka
River length, km	35	32	42
No. of wastewater inputs	6	7	1
Population served by these inputs	163,000	90,000	2,200,000
Mean flow, m ³ /s	3.0	4.2	1.7
Maximum NH ₄ -N concentration, mg/l	6.0	1.2	80.0
Maximum BOD concentration, mg/l	9.0	3.5	60.0
Maximum DO concentration, mg/l	8.5	10.5	6.0
Maximum NO ₃ -N concentration, mg/l	12.5	4.0	16.0

Crabtree *et al.* (1986) used the Qual 2EU model to simulate the River Blackwater. They found that Qual 2EU gave better results for BOD, DO and nitrate-nitrogen, but was worse for ammoniacal-nitrogen, which may be due to Qual 2EU using interactions with algal growth rather than bacteria. However, they concluded that neither model does particularly well at modelling nitrate-nitrogen, the most important variable.

6.3- APPLICATION OF THE TWO MODELS TO THE RIVER ZARKA:

The river water quality data of the River Zarka (appendix A2), obtained during the sampling period from May 1990 to January 1992, and during spring of 1993, were implemented in the simulation by both models. Data of the first upstream measuring site (site 2), taken as the first river reach, were used as initial inputs to the system, with the resulting outputs implemented as inputs to the next reach. Temperature, velocity, geometry and flow rate of the Zarka were used to find physically-based

coefficients. The assumptions of both models (Casapeiri *et al.*, 1978, and Van-Benchoten *et al.*, 1984) were used in the application for the purpose of comparison assuming each reach to be a well-mixed reactor. A flow chart representing the simulation procedure can be seen in figure (6.1).

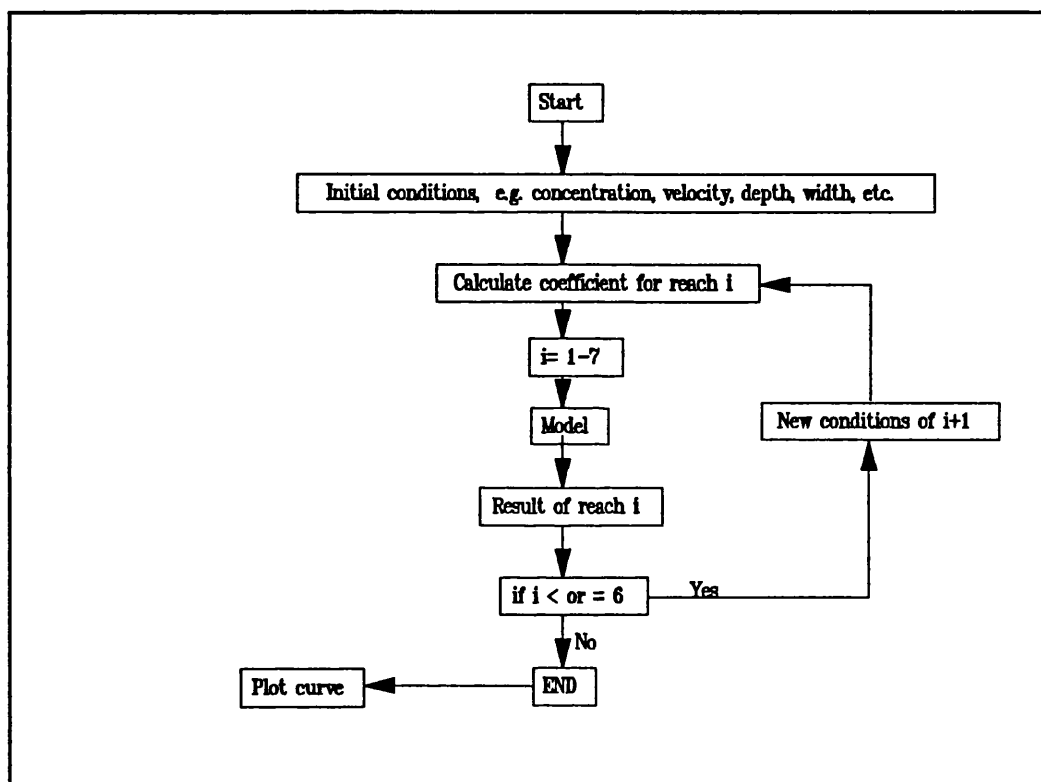


FIGURE 6.1: Simulation flow chart of the two models as applied to the River Zarka.

Before commencing the application a few assumptions had to be made when applying each system, either because of the lack of data or the confusing layout of the model equations as described in section (2.4.3).

- In Qual 2EU, the rate coefficients were corrected to temperatures of the Zarka using the Streeter-Phelps constant of 1.047 (ncasi, 1980 and

Crabtree *et al.*, 1986). While the temperature correction coefficient used by the Blackwater model is included in the relevant equation (Crabtree *et al.*, 1986, and Knowles *et al.* 1978).

- In Qual 2EU, the expression describing the rate of oxygen due to algal respiration was taken as described by Van-Benschoten *et al.* (1984):

$$d[DO] / dt = -\alpha_4 \rho A \quad (6.1)$$

where

α_4 is the ratio of oxygen uptake per unit of algae respired,

ρ is rate of algal respiration, day^{-1} , and

A is algal biomass, mg/l

While Crabtree *et al.* (1986) took ρ as P (concentration of orthophosphate, mg/l).

- The ultimate biochemical oxygen demand (uBOD) in both models was calculated by using BOD_5 values and assuming a rate coefficient of 0.23 day^{-1} (ncasi, 1980), while for the River Zarka simulation, measured uBOD values were used in the relevant equation.
- The maximum growth rate of algae (μ) was taken as 2.3 day^{-1} . Then the local growth rate of algae was calculated using the following formula, (Brown *et al.*, 1987):

$$\mu = \mu_{\max} \frac{N}{N+K_N} \frac{P}{P+K_P} \frac{1}{\lambda h} \ln \frac{K_L+L}{K_L+L \exp(-\lambda h)} \quad (6.2)$$

where:

μ_{\max} : maximum specific growth rate for algae, day⁻¹

N: local concentration of Nitrate-N, mg/l

P: local concentration of orthophosphate, mg/l

L: local light intensity at net solar radiation, cal/cm².min

λ : light extinction coefficient = 0.043, base e

h: mean depth of flow, m

K_N , K_P , and K_L are empirical half saturation coefficients for NO₃, PO₄ and light intensity, respectively.

- The benthic source rate for ammonia nitrogen taken as $\alpha_1 = 0.29$ mg/m².day, but the benthic ammonia-N coefficient was $\alpha_3 = 0.0$ mg/m².day as assumed by Van-Benchoten *et al.*, 1984).

Figures (6.2, 6.3, 6.4 and 6.5) illustrate the application of the two models to the River Zarka. In figure (6.2), the measured BOD falls dramatically after site 6 (17 km) where the river takes a shallower and wider route allowing more sedimentation, hence more settleable BOD in addition to the tributary dilution effect. The Blackwater model failed to simulate BOD concentrations since the model assumes that settling of suspended matter will take place only at velocities less than 0.2 m/s and resuspension of suspended matter will take place at velocities greater than 0.4 m/s (equations 2.17 and 2.18). While in the River Zarka, the average velocity is 0.46 m/s before site 6,

and 0.39 m/s after site 6 with an overall average velocity of 0.43 m/s. At these velocities, which all fall within the second range of the model, the suspended matter will always be suspended (according to Blackwater model), whereas the measured rate of settling of total suspended matter in River Zarka was 0.01 g/km (section 5.4.7). Hence even at the higher velocities, some suspended matter will settle in the Zarka.

The Qual 2EU model (figure 6.2), succeeded in simulating BOD for the first 17 km (until site 6) but failed thereafter, as the river changes its width and depth and accordingly velocity. The model, does not directly include these factors as described in equation (2.11). However, the model requires an input forcing function which responds to the environmental and hydrological characteristics of the river. Although, changes due to other source inputs like the tributary were considered, Qual 2EU model still assumes a low BOD decay rate.

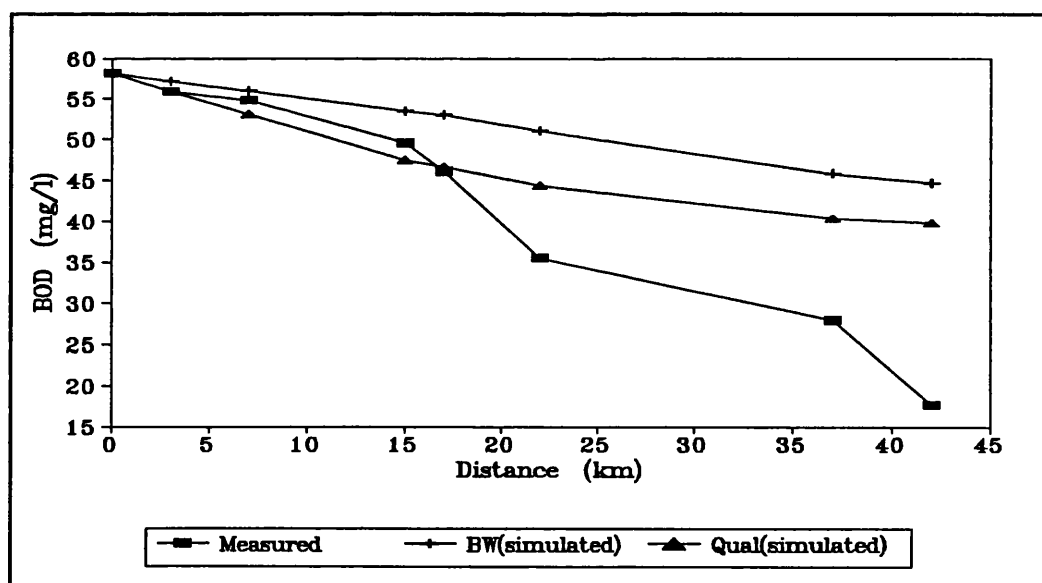


FIGURE 6.2: Measured and simulated BOD of the River Zarka by the Blackwater and Qual 2EU models.

Simulation of river dissolved oxygen was the most ineffective, since both models have failed completely to predict dissolved oxygen behaviour (figure 6.3). The Blackwater model uses 7 equations (equations 2.23 through 2.32) to compensate for oxygen inputs and outputs, (two of these equations were excluded prior to the simulation since they do not apply to the Zarka, namely equation (2.25) which allows for waterfalls and weirs, and equation (2.29) which accounts for plant respiration, the Zarka is known to be free of any weirs and waterfalls, and it is also without any plant or fish life. The reaeration rate and the air saturation value described in equations (2.23 and 2.24) depend on temperature, velocity, river depth and some empirical factors of unknown origin. This might be true for average quality fresh water, but these equations do not allow for water salinity which is known to be high in the Zarka (425 mg l^{-1} as Cl^{-}), or molecular diffusion due to high suspended solids load ($1000\text{-}1500 \text{ mg l}^{-1}$).

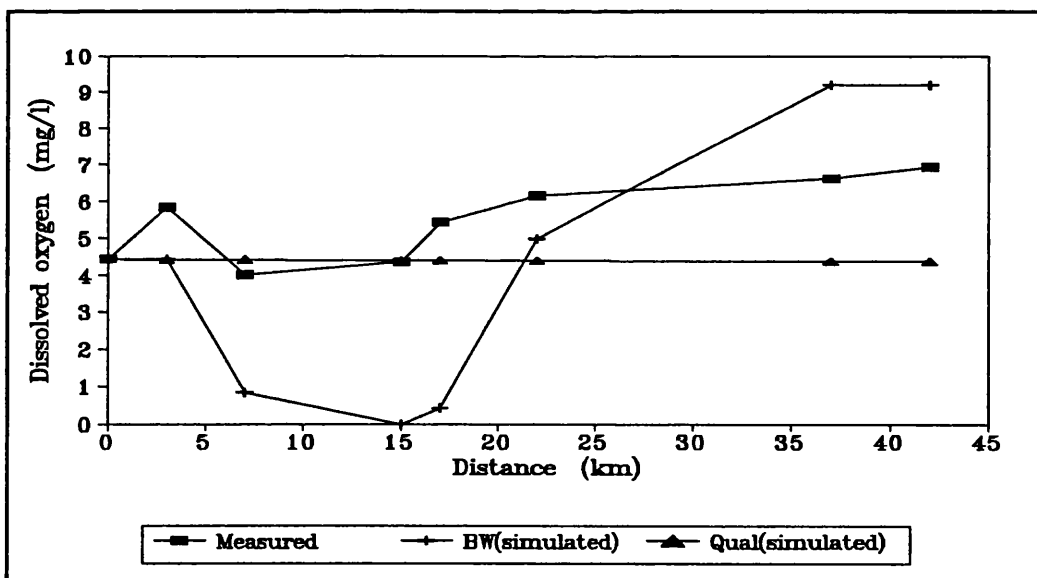


FIGURE 6.3: Measured and simulated dissolved oxygen of the River Zarka by the Blackwater and Qual 2EU models.

River velocity is an important factor in determining quantities of formed sediments along the river (section 5.4.5), and in addition the Zarka, as a shallow river, can be easily affected by floods which take place two or three times each year. This results in washing out all deposited sediments that had been formed during the preceding low flow period, that means an implementation of a fixed value to account for benthic oxygen demand is not correct.

The photosynthetic aspect of dissolved oxygen is related to light intensity and depth as in equation (2.31) which suggests that oxygen concentration due to photosynthesis increases with light intensity and decreases with depth. It was suggested in section (5.4.3) that high light intensities over the Zarka had an adverse effect on the photosynthetic activity of the river by photoinhibition. If equation (2.31) is to be considered for the Zarka, then high light intensities should be accompanied by high photosynthesis which in practice was completely the opposite.

However, oxygen levels modelled by the Blackwater model recover after site 6, but again it assumes a high oxygen increase. Although most of the above discussion applies to the Qual 2EU, this model does not limit the user with predefined equations of reaeration, air saturation coefficient, etc., but the overall model uses 28 coefficients, 23 of which are literature-based, 4 assumed and only one coefficient directly monitored (Van-Benschoten *et al.*, 1984). Modelled dissolved oxygen by Qual 2EU assumes that oxygen sources and sinks are almost equal, consequently predicted DO was followed in more or less a horizontal line.

The Qual 2EU model succeeded to a certain degree in simulating the change in ammonia-nitrogen as illustrated in figure (6.4). However, the reason behind that is because the local respiration of algae (p) was assumed, as suggested by the model, to be 5% of the maximum growth (μ), (Van Benschoten *et al.*, 1984) since no specific measured values are available, although experimental work on algae suggest that it is much less than this value, as discussed in section (5.4.3 and 5.4.4), according to low algal respiration in respect to high algal biomass. The Blackwater model failed in predicting the change in ammonia-nitrogen after site 6, since this model relates the change in ammonia to the change in bacterial biomass (taken as mg/l of *Nitrosomonas europaea*) which is in turn related by an empirical formula to the concentration of ammonia-nitrogen (equation 2.20). This model only predicted the first part of the river when there was no significant change in the concentration of ammonia-nitrogen (from 80 to 75 mg/l $\text{NH}_4\text{-N}$).

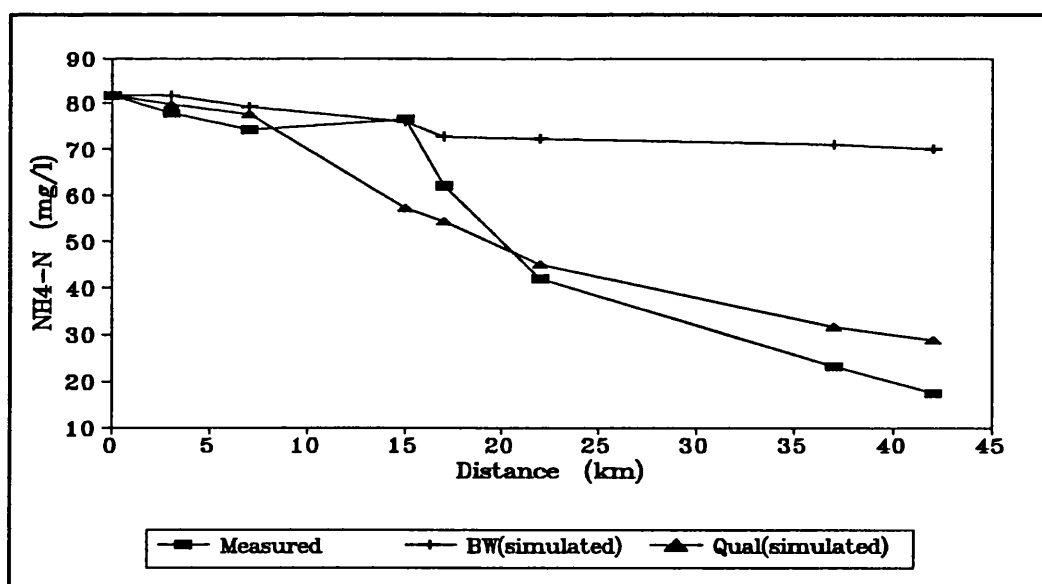


FIGURE 6.4: Measured and simulated ammonium-nitrogen of the River Zarka by the Blackwater and Qual 2EU models.

The Blackwater model relates the change in nitrate-nitrogen to only the change in ammonia-nitrogen (equations 2.21, and 2.22), and since it suggested little change in ammonia-nitrogen as in figure (6.4), the result will automatically be little or no change in nitrate-nitrogen (figure 6.5). However, the model includes a term to allow for loss of nitrate-nitrogen by denitrification, but this process is known to take place after nitrification has taken place and under anoxic conditions.

The Qual 2EU model predicted a continuous increase in the amount of nitrate-nitrogen as it related change in nitrate-nitrogen to change in nitrite-nitrogen and algal respiration, which in turn is related to the algal biomass expressed in terms of chlorophyll concentration. However, it was still not adequate as it was shown in section (5.4.3) that chlorophyll concentration of the Zarka is misleading since it suggests high algal activity while in practice it was inhibited by river toxicity and by photoinhibition.

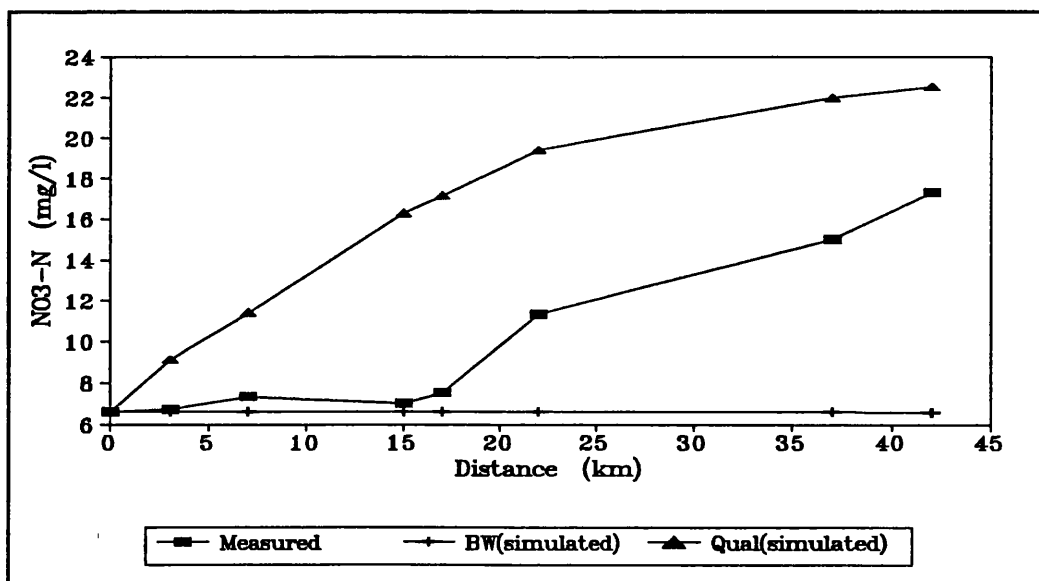


FIGURE 6.5: Measured and simulated nitrate-nitrogen of the River Zarka by the Blackwater and Qual 2EU models.

The next step was to use both models by introducing the measured values of River Zarka as inputs and as outputs, and then recalculate the resulting rates and coefficients. This was only done for comparison purposes as the model should always be modified to fit the problem and not vice versa. A flow chart representing the calculation procedure can be seen in figure (6.6).

Tables 6.2 and 6.3 list the rate constants and coefficients used by both the Blackwater and Qual 2EU models and those calculated for the River Zarka system.

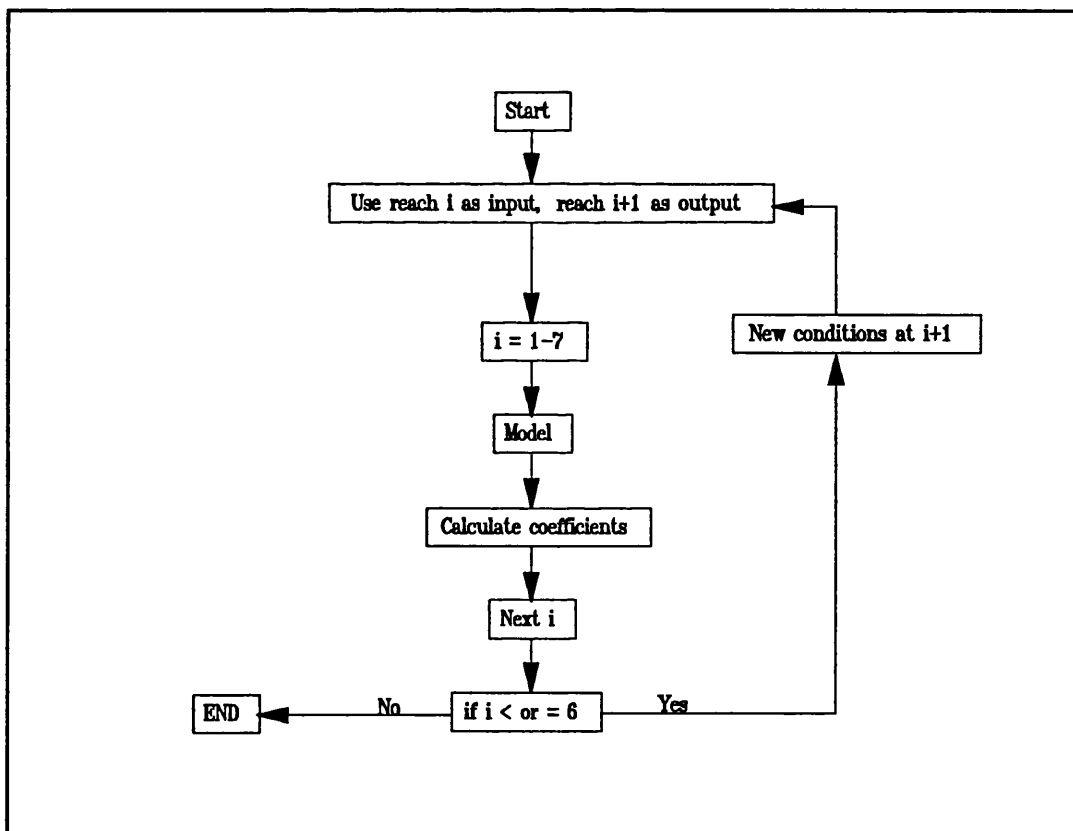


FIGURE 6.6: Flow chart for calculating model coefficients for River Zarka using measured data as inputs and outputs.

TABLE 6.2: Parameters and coefficients used by the Blackwater model and the Zarka River

Parameter	Blackwater	Zarka calculated
K_B BOD decay constant (min^{-1})	1.39×10^{-4}	8×10^{-4}
k_2 rate constant given by equation (2.22), (unitless)	4.3	0.17
K_R reaeration rate constant given by equation (2.24) (min^{-1})	0.005	0.019
K_A constant depending on the type of the river bed, e.g. gravel, mud, etc., (unitless)	0.29-3.0	54.1
K_s settling rate constant (mgm^{-1})	0.01	5.90
B_N a measure of the amount of <i>Nitrosomonas europaea</i> in the river bed (unitless)	1.0-4.0	1.5-6.9

TABLE 6.3 Coefficients used by the Qual 2EU model and the Zarka river.

Coefficient	Qual2EU model	Zarka calculated
k_1 rate of change in BOD (day^{-1})	0.2	0.32
k_3 coefficient for settling and scour effects (m.day^{-1})	0.0	0.41
β_1 rate coefficient for oxidation of ammonia-nitrogen (day^{-1})	0.3-2.0	0.001
β_2 rate coefficient for oxidation of nitrite-nitrogen (day^{-1})	2.0	0.02

The above two tables indicate that implementation of the measured concentrations of the modelled parameters into both models will result in some cases, (e.g. river bed denitrification characteristics as expressed by K_A , settling rate constant represented by K_s , or in the case of Qual 2EU, the rate of oxidation of ammonium, etc.), in unrealistic (according to conditions of the River Zarka) constants and coefficients. This leads to inadequate modelling the Zarka and confirms the need to consider a revised model.

6.4- CONCLUSIONS:

Applying conditions of the River Zarka to both models, using assumptions made by these models, failed partially or totally to adequately simulate the Zarka. The prime reason is the unusual nature of the river in it being highly polluted with high concentrations of ammonium, bacterial count, and algal biomass (but with low activity). Moreover, the River Zarka is a warm shallow fast flowing river with an average depth of 40 cm, an average velocity of 0.43 m/s and a width ranging between 3-17 meters.

The major factors affecting the degree of closeness of predictive fit are the rate of nitrification process, the assimilation of nitrate-N by aquatic plants (the Zarka is known to be free of any plant life), the extent of ion exchange with benthic sediment, the agricultural return flow and the assumptions adopted in model formulation (Al-Layla *et al.*, 1989).

High initial concentrations of ammonia-N, bacterial count and BOD as well as low concentrations of DO indicate the high state of pollution of the river. Considering other parameters, such as chlorides, phosphate, chlorophyll, TOC and COD, the river can be viewed as a semi-treated effluent rather than a fresh-water stream, and should be modelled accordingly. The need for a specific model can be seen by considering the following points:

- 1- The main source of the river is an unconventional source, quantitatively and qualitatively overloaded wastewater stabilization ponds,

- 2- The sudden river configuration change after 17 km, which affects reaeration.
- 3- Non-frequent chlorination of the water, resulting in high bacterial biomass.
- 4- River bed sediment flushing twice or more during the wet season,
- 5- High chlorophyll concentration but low algal activity,
- 6- High solar energy radiation over a shallow water,
- 7- Short residence time due to the length of the river,
- 8- Low inflow from the less polluted tributary,
- 9- High bacterial concentrations.

CHAPTER SEVEN

THE ZARKA MODEL

7.1- INTRODUCTION:

It was shown in chapter Six that a general comprehensive model, like the Qual 2EU does not represent a unique system like the River Zarka, which is a highly polluted river flowing in a semi-arid region. The river also falls under other conditions that require specific factors to be taken into consideration: it flows in a region with high light intensities that can affect algal growth by photoinhibition; contains high bacterial biomass; has a shallow route which is highly responsive to the surrounding environment; and there is the possible effect of heavy metal toxicity.

Therefore, the need arose to design a model that takes these factors into consideration by using experimental work to identify important points specific to the Zarka and similar rivers in the region.

Such a model is described in the following sections. The mathematical part was constructed using Quattro-Pro for Windows software (Borland 1992). Coefficients (other than measured ones) were found by using an optimization technique to minimize the error between calculated and measured values. The technique used was to find the sum of the square of the error between measured and modelled and then set the solution to minimize the sum as it to approach zero. The computer tried 1000 iterations to find the unknowns. The description of model mathematics is listed in Appendix (A3).

The novelty of the model stems from the fact that it is the first of its type that combines the two major factors affecting nitrification, (i.e. bacterial and algal biomass) in a real river system under the conditions of the River Zarka. Although, bacterial and algal biomass activities in nitrification processes have been studied separately by many researchers, they have not been combined and applied to a real river system before. In addition, algal activity is represented here by the ratio of maximum to minimum oxygen concentrations in diurnal DO rather, than by using algal biomass, as this proved to be misleading in the case of the River Zarka. This model, which will be called the Zarka Model, constitutes a solid base for any future research which will take into consideration findings that arose during the construction of this model, (e.g. determination of type of toxicity and degree of photoinhibition).

The overall model construction including all modelled parameters can be seen in figure (7.1), which shows sources and sinks of these parameters and their interaction with each others. Table (7.1) shows initial values used in the model formulation. These values represent the average of 24 monthly samples which were collected during day time (except for diurnal DO).

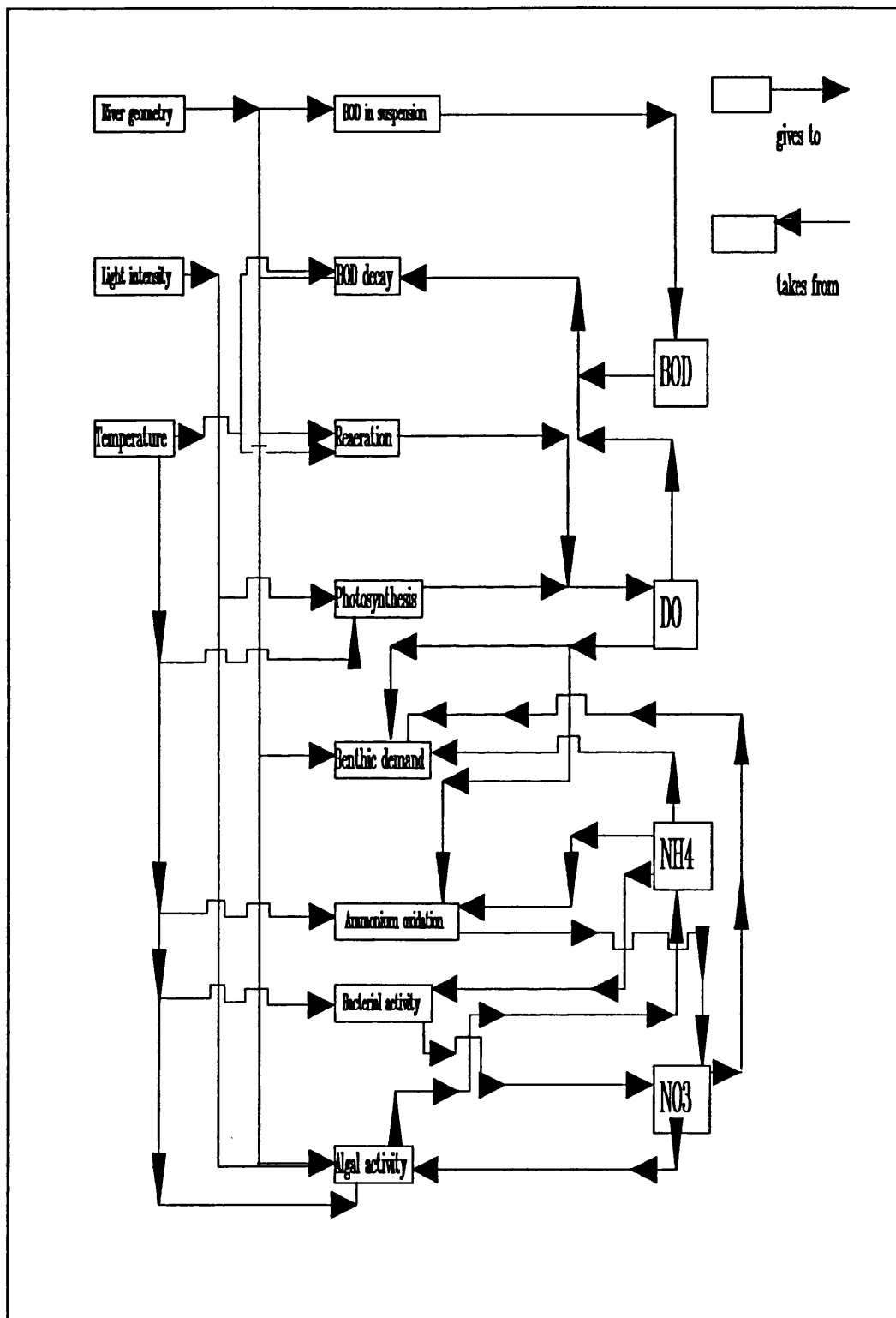


FIGURE 7.1: Zarka model parameters interaction flowchart.

TABLE 7.1: Data used in Zarka model construction.

PARAMETER	St. Error of test	REACH 1			REACH 2			REACH 3			REACH 4			REACH 5			REACH 6		MAX	REACH 7		
		AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN		AVG	MIN	MAX
Depth (m)	± 0.01	0.75	0.70	0.80	0.5	0.45	0.55	0.45	0.4	0.5	0.5	0.45	0.55	0.22	0.18	0.25	0.29	0.25	0.32	0.25	0.21	0.28
Length (km)	± 0.10	3.00	3.0	3.0	7	7	7	15	15	15	17	17	17	22	22	22	37	37	37	42	42	42
pH value	± 0.2	8.0	7.52	8.4	8.2	7.8	8.6	8.0	7.6	8.3	7.7	6.85	8.52	7.8	7.0	8.5	7.9	7.2	8.5	7.8	7.3	8.3
Temperature°C	± 0.1	16.4	6.7	26.0	17.8	8.4	27.2	17.7	7.5	27.8	18	6.6	29.3	17.7	6.5	28.9	17.5	6.2	28.7	17.6	6.1	29.1
DO (mg/l)	± 0.05	7.0	4.0	9.9	5.5	2.1	8.9	4.05	2.1	6.0	5.7	2.6	8.8	6.4	3.9	8.8	6.7	4.5	8.9	6.6	3.7	9.5
Cl (mg/l)	± 5	351	277.9	424.2	351	277.9	424	387	305	468	400	333	468	408	333	484	372	295	448	403	330	476
BOD (mg/l)	± 0.5	67.5	25	110	63	25	100	53.5	19.5	87.4	48	15	80.1	34.3	5.0	63.6	28.5	5.0	52	23	2.0	44
Chlorophyll "a" (µg/l)	± 10	557	200	914	533	58	1009	386	173	600	324	19.8	630	257	145	370	153	38	267	160	40	281
Total count *	± 0.1	200	100	300	70	55	70	200	180	220	80	90	70	80	30	28	32	8	12	4	3	5
NO3-N (mg/l)	± 0.1	5.6	2.1	9.0	8.6	3.2	14.0	16.6	2.5	14.1	9.4	3.4	15.4	11.9	6.0	17.8	16.9	7.3	26.5	18.5	7.0	30.0
NO2-N (mg/l)	± 0.05	1.4	0.0	2.7	1.8	0.0	3.6	4.7	0.0	9.4	4.9	0.1	9.7	4.2	0.1	8.3	3.5	0.3	6.6	3.3	0.1	6.4
NH4-N (mg/l)	± 0.1	82.9	60.2	105.6	78.1	52.2	104	173	57.4	115	66.1	46.3	85.9	49	29.4	68.9	27.5	10	45	23.4	2.8	44
Flow rate,m ³ /s	± 0.05	1.05	0.9	1.2	0.37	0.9	1.2	1.05	0.9	1.2	2.5	0.9	4.1	2.5	0.9	4.1	2.5	0.9	4.1	2.5	0.9	4.1
Velocity (m/s)	± 0.01	0.39	0.33	0.45	0.5	0.4	0.6	0.45	0.4	0.5	1.0	0.36	1.65	0.5	0.2	0.8	0.55	0.2	0.9	0.8	0.3	1.3

*x10⁵(cfu/ml)

7.2- MODEL ASSUMPTIONS:

Prior to modelling, assumptions must be made to simplify the natural system in order to represent the model mathematically, although simplification due to assumptions must not over-look important points.

The assumptions used can be summarised as follows:

- The distance between two consecutive sites were considered to be one reach, therefore, the whole river was divided into 7 reaches.
- Each reach was assumed to be a Continuous Stirred Tank Reactor (CSTR).
- No point source inputs other than the tributary were included in the system as they were regarded insignificant to the overall system.
- The data applied in constructing the model are the averages of three years data (including the specific experiments to find model parameters). The effect of change in temperature (as at different seasons) was included in the model as a correction factor to the rates and coefficients of the model.
- The particle size of the suspended solids was taken in the range 0.25-0.3mm since no data are available on the actual particle size (the effect of using larger particle size (0.4-0.6mm) was also modelled and found to insignificantly affects the reaeration rate).
- Nitrifiers were assumed to constitute a fixed proportion of the total bacterial count.
- Temperature correction factors are included in each model equation

where applicable.

7.3- THE ZARKA MODEL:

The major parameters affecting nitrification were studied in Chapter Five, where different relationships were found to correlate between these parameters and nitrification in the Zarka. In Chapter Six the inadequacy of other systems to represent the River Zarka was studied. However, the Qual 2EU model, as the best of the two used, is again included in this chapter to represent the differences between Qual 2EU and the constructed Zarka model. Parameters that are affected by nitrification in the River Zarka are described in the following sections. Model constants and coefficients are listed in table (7.2).

The Zarka model was developed with data taken at average temperature of around 20°C. Therefore, a range from 5-30°C was tested using the model. The temperature correction factor can be written as:

$$k_T = k_{(20)} * \theta^{(T-20)} \quad (7.1)$$

where:

k_T = rate coefficient at temperature T°C

$k_{(20)}$ = rate coefficient at 20°C

θ = temperature correction factor, dimensionless

T = Temperature, °C

The coefficient for temperature expressions are:

1- BOD decay rate, $\theta = 1.016$

2- Oxygen reaeration rate coefficient, $\theta = 1.061$

3- Ammonium decay rate, $\theta = 1.035$

- 4- Nitrate production rate, $\theta = 1.118$
- 5- Algal activity coefficient for NH_4 and NO_3 , $\theta = 1.047$ (Crabtree *et al.*, 1986)
- 6- Bacterial activity coefficient for NH_4 and NO_3 , 1.047 (Crabtree *et al.*, 1986)
- 7- Saturation dissolved oxygen concentration, temperature related in equation (7.12).
- 8- Benthic oxygen demand coefficient, 1.061

7.3.1- BIOCHEMICAL OXYGEN DEMAND (BOD):

Biochemical Oxygen Demand (BOD) reactions are the result of the reduction of carbonaceous matter by a heterotrophic group of organisms, when also simultaneously nitrogenous matter is converted to oxidized nitrogen compounds by specific nitrifying bacteria. Two factors constitute the overall BOD model and were found to be affecting the removal of BOD: the decay in BOD due to aeration, and resuspension of BOD due to turbulence and velocity. These two factors can be represented in the following equations and the resulting model is plotted in figure (7.2):

The overall BOD model is described as follows, equation (7.1).

$$\frac{d[BOD]}{dt} = - (1.016^{(T-20)} k_1 [L]) + k_3 [L] \quad (7.2)$$

where:

$d[BOD]/dt$ = rate of BOD removal, $\text{mg l}^{-1} \text{min}^{-1}$

k_3 = coefficient for BOD in suspension, min^{-1} (temperature invariant)

$[L]$ = ultimate BOD, mg l^{-1}

T = temperature, $^{\circ}\text{C}$.

k_1 was found from measured values of BOD_5 and ultimate BOD (L) by using the following formula (Arceivala, 1981), which is frequently used to

represent measured values:

$$k_1 = \ln \left(1 - \frac{[BOD_5]}{[L]} \right) / t \quad (7.2.a)$$

where:

t = time of BOD incubation, 5 days

k_1 = BOD rate coefficient at 20°C (base e), day⁻¹

$[BOD_5]$ = five day BOD, mg l⁻¹

The BOD decay rate coefficient for the Zarka was found to be $3 \times 10^{-4} \text{ min}^{-1}$, while it was $1.4 \times 10^{-4} \text{ min}^{-1}$ for both, the River Winooski (Van-Benschoten *et al.*, 1984) used in the Qual-2EU and the River Blackwater (Knowels *et al.*, 1978) applications. Figure (7.2) shows that the Zarka model succeeded in simulating the River Zarka.

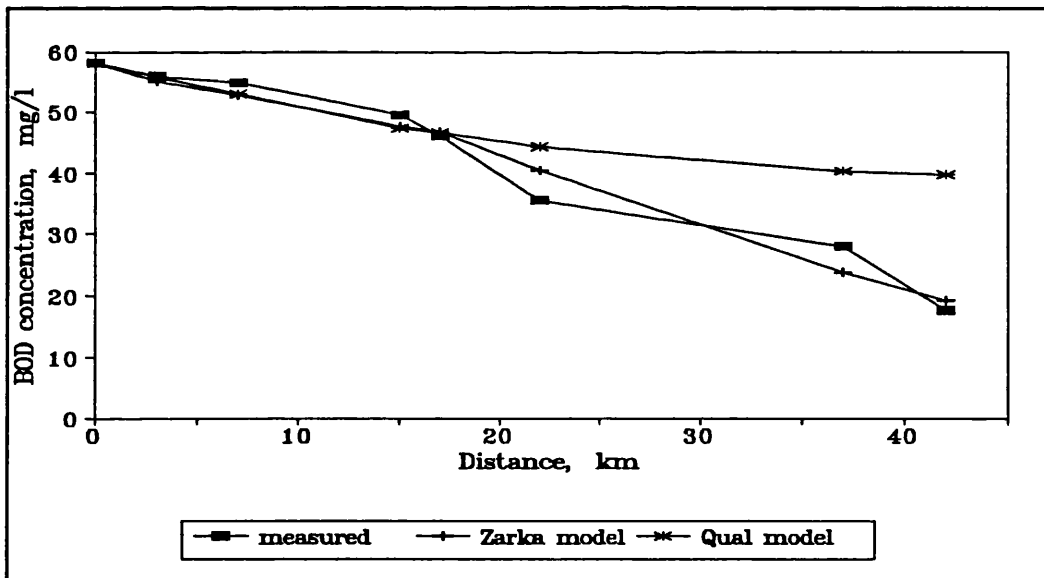


FIGURE 7.2: Measured and simulated Biochemical Oxygen Demand (BOD) by the Zarka and Qual 2EU models.

7.3.2- AMMONIUM NH_4^+ :

The high initial ammonium concentration resulted from the type of wastes being discharged into the system through the Waste Stabilization Ponds (WSP). These do not allow for nitrification to take place, and affect the river water suitability for

aquatic life, resulting in polluted water with no fish or plant lives. The main aim, in terms of purification, is nitrification to reduce ammonium to nitrate form which can be used by plants, or can be denitrified to molecular nitrogen, which reduces the possibility of eutrophication.

As described in chapter five, ammonium concentrations are affected by physical properties as well as bacterial and algal activity. Other models, such as Qual 2EU used algal biomass as the main influence on nitrification, while on the other hand the Blackwater model used bacterial biomass. In the Zarka model, both factors were combined such that ammonium concentrations can be described in the following equations and the over all ammonium model is described in equation (7.3).

$$\frac{d[NH_4]}{dt} = - (Eqn. 7.4) + (Eqn. 7.5) - (Eqn. 7.6) - (Eqn. 7.7) \quad (7.3)$$

where:

1- due to bacterial activity as found from chapter five, equation (5.11):

$$= 1.047^{(T-20)} * (a_1 [X]^{b_1} - a_2) \quad (7.4)$$

where:

[X] = total bacterial concentration, cfu.ml⁻¹

a₁=0.18, a₂=0.17, b₁=0.017 (correlation factors, dimensionless)

2- due to algal activity:

$$= 1.047^{(T-20)} * (r_1 \cdot R \cdot C_1) \quad (7.5)$$

where:

r₁= algal source rate of ammonium, mg l⁻¹ min⁻¹

R = ratio of maximum oxygen to minimum oxygen concentration in a diurnal DO, dimensionless

C_1 = correction constant to allow for photoinhibition and toxicity, (a value between 0 and 1), dimensionless.

3- due to benthic sources of ammonium:

$$= r_3 \cdot W \cdot A \cdot C_2 \quad (7.6)$$

where:

r_3 = benthic source rate for ammonium, $\text{mgNH}_4/\text{kg sediment l}^{-1}\text{min}^{-1}$

W = weight of sediment per square metre, kgm^{-2}

A = cross-sectional area covered by sediment, m^2

C_2 = Correction coefficient to allow for conditions of river bed according to season before or following a flood, dimensionless

4- due to ammonium oxidation:

$$= 1.047^{(T-20)} \cdot \alpha_1 [\text{NH}_4] \quad (7.7)$$

where

α_1 = ammonium oxidation rate coefficient (reach specific), min^{-1}

$[\text{NH}_4]$ = concentration of ammonium, mg l^{-1}

This is unique in that algal activity in terms of oxygen production rather than algal biomass has been used to represent the effect on nitrification. The main reason for adopting this approach is because algal biomass, in terms of chlorophyll concentration or dry cell weight proved to be misleading in the Zarka, as other factors are believed to adversely affect algal activity e.g. photoinhibition and water toxicity (which will only affect their activity without a substantial loss in their bulk mass in agreement

with the work of Barber (1987)).

In addition, in general benthic oxygen demand or benthic source of ammonium has been previously expressed in terms of the cross-sectional area of the reach, or the depth of the sediment. In this study, actual measures of sediment weight (of 0.25-0.3mm particle size) and area are combined to reflect benthic demand or source. Moreover, this allows for conditions following winter floods which result in flushing away of sediments accumulated during the previous low flow period.

The resulting ammonium model is represented in figure (7.3) together with application of Qual 2EU. This figure shows that the Zarka model successfully represented the River Zarka. Qual 2EU also represented the system, but only by adopting the respiration rate of the River Winooski (due to unavailable Zarka value) which is much higher than that of the Zarka (as found by experimental work on algal activity in chapter five). Qual 2EU value compensated for the loss in algal activity due to photoinhibition.

7.3.3- NITRATE NO_3^- :

Nitrate, as one of the major products of nitrification is in a utilizable form for plant life. However, high nitrate concentrations can lead to eutrophication of receiving waters, as has already occurred in the King Talal Dam (KTD) downstream of the River Zarka (Salameh *et al.*, 1987; and Abumoghli, 1991). Nitrate can be reduced to molecular nitrogen by denitrification if other conditions are suitable, (e.g. anaerobic environment). Nitrate levels were found to be more affected by bacterial activity than ammonium concentration and can be best represented by a MRS (modified reciprocal

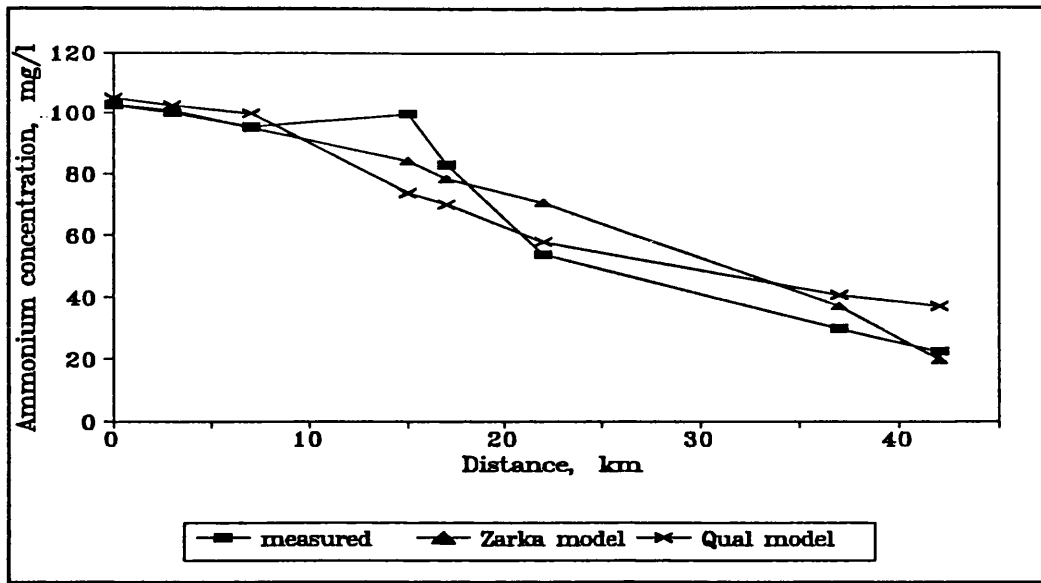


FIGURE 7.3: Ammonium concentration as modelled by the Zarka and Qual 2EU models.

straight line) model, as discussed in chapter Five, equation (5.3). However, other factors affect nitrate production such as algal activity, benthic demand and ammonium reduction. These factors can be combined in a model as in the following equation:

$$\frac{d[NO_3]}{dt} = (Eqn. 7.9) - (Eqn. 7.10) + (Eqn. 7.11) - (Eqn. 7.12) \quad (7.8)$$

where:

1- due bacterial activity as in equation (5.3):

$$= 1.047^{(T-20)} * \frac{a_3 b_3 [X]}{a_3 + b_3 [X]} \quad (7.9)$$

where:

$[X]$ = total bacterial concentration, cfu.ml⁻¹

$a_3 = 0.065$, $b_3 = 1.1 \times 10^{-5}$ (correlation constants, dimensionless)

2- due to algal activity:

$$= 1.047^{(T-20)} * r_2 \cdot R \cdot C_3 \quad (7.10)$$

where:

r_2 = algal source rate for nitrate, $\text{mg l}^{-1} \text{min}^{-1}$

R = ratio of maximum oxygen to minimum oxygen concentration in a diurnal DO, dimensionless

C_3 = correction constant to allow for photoinhibition and toxicity, dimensionless.

3- due to ammonium oxidation:

$$= 1.047^{(T-20)} * \alpha_2 \frac{d[NH_4]}{dt} \quad (7.11)$$

where:

α_2 = stoichiometric equivalent for the oxidation of ammonium into nitrate, $\text{mgNO}_3/\text{mgNH}_4$

$d[NH_4]/dt$ = rate of ammonium decay, $\text{mg l}^{-1} \text{min}^{-1}$

4- due to benthic source:

$$= r_4 \cdot W \cdot A \quad (7.12)$$

where:

r_4 = benthic source rate for nitrate, $\text{mgNO}_3/\text{kg sediment.l}^{-1} \cdot \text{min}^{-1}$

W = weight of sediment per square metre, kg m^{-2}

A = cross-sectional area covered by sediment, m^2

Nitrate has been in the literature generally related to ammonium or nitrite oxidation, and algal activity as in Qual 2EU, or only to the oxidation of ammonium, as in the Blackwater model. Using Qual 2EU and considering only these factors for the Zarka,

resulted in a failure in representing the system, as can be seen from figure (7.4), whereas the Zarka model successfully represented the measured data.

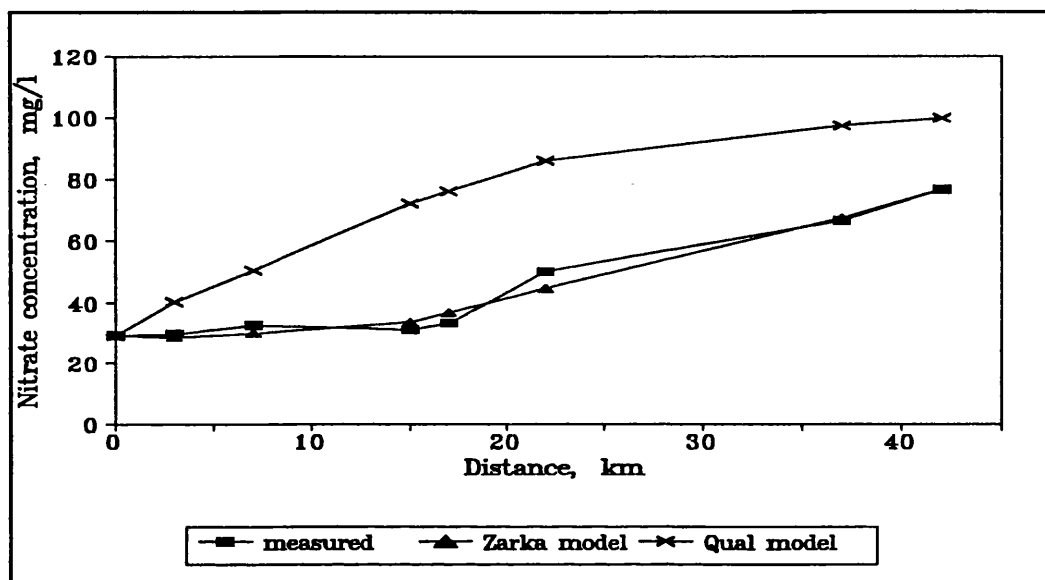


FIGURE 7.4: Measured and simulated nitrate concentrations by the Zarka and Qual 2EU models.

7.3.4- DISSOLVED OXYGEN (DO):

A stream has a natural capacity for purifying itself by oxidizing biodegradable wastes, with the oxygen required to complete the reactions obtained from the stream water. The amount of dissolved oxygen contained in stream water is dependent primarily upon two factors; (1) DO contained and produced within the stream water and (2) DO added to the system from joining waters or through aeration. These two sources are subject to sources and sinks which are highly dependent on the nature of the stream and the surrounding environment. However, these factors may vary in their importance between one stream and another depending upon the state of the stream, (e.g. oxygen deficit, temperature, salinity, stream velocity and slope, in addition to the various oxygen demands that may be involved like benthic, chemical and biochemical oxygen demand).

The sources and sinks of oxygen in the River Zarka can be described as follows:

$$\frac{d[DO]}{dt} = (Eqn. 7.14) - (Eqn. 7.15) + (Eqn. 7.16) - (Eqn. 7.17) -$$

$$(Eqn. 7.18) \quad (7.13)$$

where:

1- due to reaeration:

$$= k_2 * ([DO_s] - [DO]) \quad (7.14)$$

where:

k_2 = *in-situ* reaeration coefficient (base e), min^{-1} , determined using the following equation (Churchill *et al.*, 1962 as cited by Zison *et al.*, 1978), which is generally considered the best equation to represent measured data:

$$k_2 = \{ \ln ([DO_{d1}] - [DO_{d2}]) / t \} \quad (7.14.a)$$

where:

$[DO_{d1}]$ = oxygen deficit ($[DO_s] - [DO]$) at upstream reach, mg l^{-1}

$[DO_{d2}]$ = oxygen deficit at downstream reach, mg l^{-1}

$[DO]$ = concentration of oxygen, mg l^{-1}

t = time of travel, min^{-1}

$[DO_s]$ = oxygen saturation concentration in mg l^{-1} , calculated using

the following formula (Hyer *et al.*, 1971 as cited by Zison

et al., 1978) as the best equation to represent measured data:

$$[DO_s] = 14.62 - 0.37 (T) + 0.0045 (T^2) - 0.097 (S) + 0.0021 (S \cdot T) + 0.0003 (S^2) \quad (7.14.b)$$

where:

T = temperature, °C

S = salinity, ppt given by the following equation (Greenberg *et al.*, 1980):

$$S = 0.03 + 0.0018 [Cl] \quad (7.14.c)$$

where:

[Cl] = chlorinity as chloride concentration, mg l^{-1}

The reaeration rate coefficient was corrected for the suspended solids load which is known to be high in the river ($1000\text{-}1500 \text{ mg l}^{-1}$), by using a relationship described by Scott (1981). This formula was based on experimental work with polystyrene with a density of (s.g. 1.04-1.08), the relationship can be represented as follows:

$$k_r = 1.063 - 0.256 \cdot \log_{10} S \quad (7.14.d)$$

where:

k_r = reaeration coefficient correction factor, dimensionless

S = suspended solids load, mg l^{-1}

The resulting correction factor was multiplied by the reaeration coefficient. Figure (7.5) shows the effect of using this relationship in improving the predicted DO curve in terms of closer fit. However, an improvement to this relationship may be made using river water with different suspended solid loads and different particle size especially in a range lower than the one used in the above relationship.

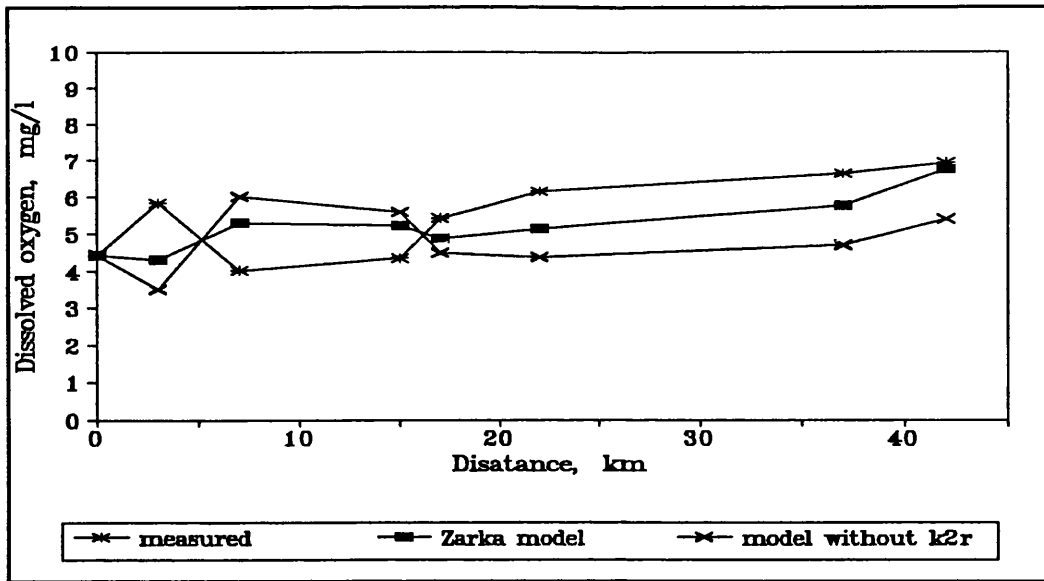


FIGURE 7.5: Improvement in predicted DO curve after adopting Scott relationship for reaeration coefficient under high suspended solids.

2- due to BOD decay:

$$= -k_1 [BOD] \quad (7.15)$$

where:

k_1 = BOD rate coefficient, min^{-1}

$[BOD]$ = concentration of BOD, mg/l

3- due to photosynthesis:

$$= 1.061^{(T-20)} * r_5 * \alpha_3 * C_4 * R \quad (7.16)$$

where:

r_5 = oxygenation rate due to photosynthesis, $\text{mg l}^{-1} \text{min}^{-1}$, found from the light/dark experiments in section (5.4.3).

α_3 = correlation coefficient, dimensionless

C_4 = Correction coefficient to allow for photoinhibition and toxicity, dimensionless

4- due to benthic oxygen demand:

$$=r_6 \cdot \alpha_4 \cdot W \cdot A \quad (7.17)$$

where:

r_6 = rate of benthic oxygen demand, $\text{mgkg}^{-1}\text{l}^{-1}\text{min}^{-1}$ (found experimentally, chapter five)

α_4 = correlation constant, dimensionless

W = weight of sediment per square metre, kgm^{-2}

A = cross-sectional area covered by sediment, m^2

5- due to ammonium oxidation:

$$=r_7 \cdot \alpha_5 \cdot [\text{NH}_4] \quad (7.18)$$

where:

r_7 = rate coefficient for ammonium oxidation, min^{-1}

α_5 = stoichiometric equivalent for ammonium oxidation

$\text{mgO}_2/\text{mgNH}_4$

$[\text{NH}_4]$ = concentration of ammonium, mg l^{-1}

The over all dissolved oxygen model is represented in figure (7.6) compared to the Qual 2EU model. Table 7.1 lists all coefficients and constants as measured for and found by the Zarka model.

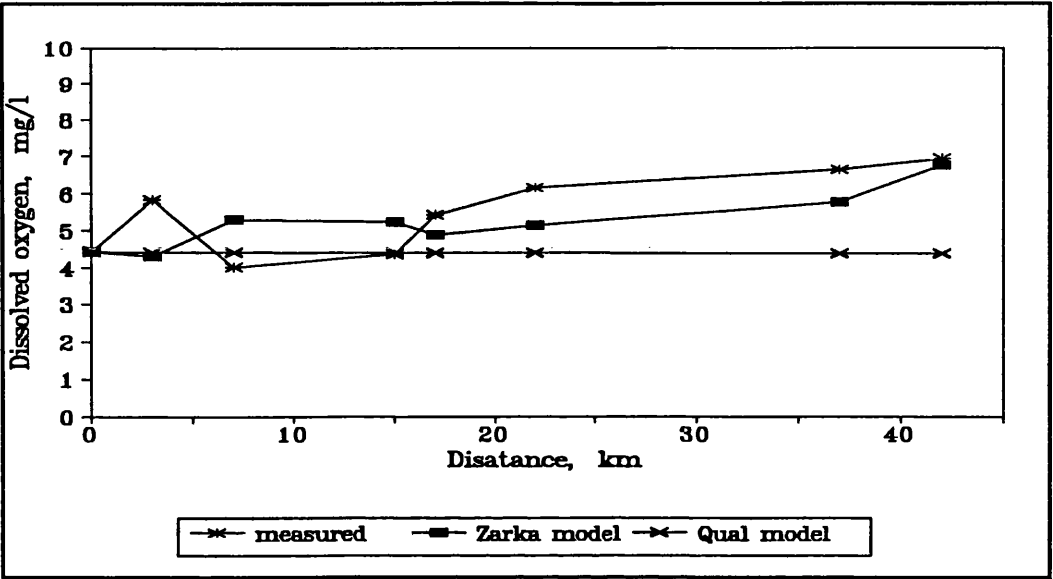


FIGURE 7.6: Dissolved oxygen concentration as measured and simulated by the Zarka and Qual 2EU models.

TABLE 7.2: Constants and coefficients for the River Zarka used by the Zarka model.

Coefficient or Constant	Description	Value
k_3	Coefficient for resuspension of BOD, min^{-1}	6×10^{-4}
r_1	Algal source rate for ammonium, $\text{mg l}^{-1} \text{min}^{-1}$	0.089
r_2	Algal source rate for nitrate, $\text{mg l}^{-1} \text{min}^{-1}$	0.038
r_3	Benthic source rate for ammonium, $\text{mg l}^{-1} \text{min}^{-1} \text{kg}^{-1}$	5.6×10^{-6}
α_1	Ammonium rate coefficient, min^{-1} (reach specific)	2.8×10^{-4} - 6×10^{-4}
α_2	Ammonium to nitrate oxidation rate coefficient, min^{-1}	9.6×10^{-6}
r_4	Nitrate benthic source rate coefficient, $\text{mg NO}_3/\text{Kg sediment l}^{-1} \text{min}^{-1}$	9.8×10^{-6}
r_5	Measured rate of oxygenation due to photosynthesis, $\text{mg l}^{-1} \text{min}^{-1}$ (reach specific)	0.001- 0.005
α_3	Oxygen photosynthetic correlation constant, dimensionless	0.181
r_6	Benthic demand correlation constant, kg^{-1}	0.0003
α_4	Measured benthic oxygen demand, (reach specific), $\text{mg l}^{-1} \text{min}^{-1}$	0.005-0.01
r_7	Ammonium oxidation rate coefficient, min^{-1}	3.8×10^{-5}
α_5	Stoichiometric ratio, $\text{mg O}/\text{mg NH}_4$	4.33
C_1	Correction constant for ammonium oxidation due to photoinhibition and toxicity, dimensionless	0-1
C_2	Correction constant for ammonium oxidation due to benthic source to account for river bed conditions following a flood, dimensionless	0-1
C_3	Correction constant for nitrate production to allow for photoinhibition, dimensionless	0-1
C_4	Photosynthetic correction constant to allow for photoinhibition, dimensionless	0-1

7.3.5- TEMPERATURE DEPENDENCE:

In chapter Five it was shown that both ammonium reduction and nitrate production rates are temperature dependent, as well as reaeration and deoxygenation rates. It was also found that rates were best corrected for temperature changes using an Arrhenius type relationship, equation (5.1). The River Zarka, as a shallow river that flows in a semi arid region can respond quickly to the surrounding environment in which change of temperature is a major factor. It is not unusual that over 24hrs, temperature changes at 10°C can occur. Its not only the diurnal temperature that is important, but also the seasonal changes in temperature (7-25°C). Therefore, it is essential to include the effect of temperature on the different constituents of the Zarka model as can be seen in the different equations representing the model.

These correction factors were used to allow for temperature change, as can be seen from figures (7.7, 7.8, 7.9 and 7.10) for BOD, ammonium, nitrate, and dissolved oxygen respectively.

The decay of biochemical oxygen demand (BOD) was slightly affected by temperature, (figure 7.7). This is because in domestic sewage (which constitutes 90% of the Zarka water) BOD is mainly in suspended and colloidal form so that removal on bioflocs is largely physical and relatively independent of temperature. Moreover, at higher BOD concentrations, BOD becomes more temperature dependent (Eckenfelder, 1989).

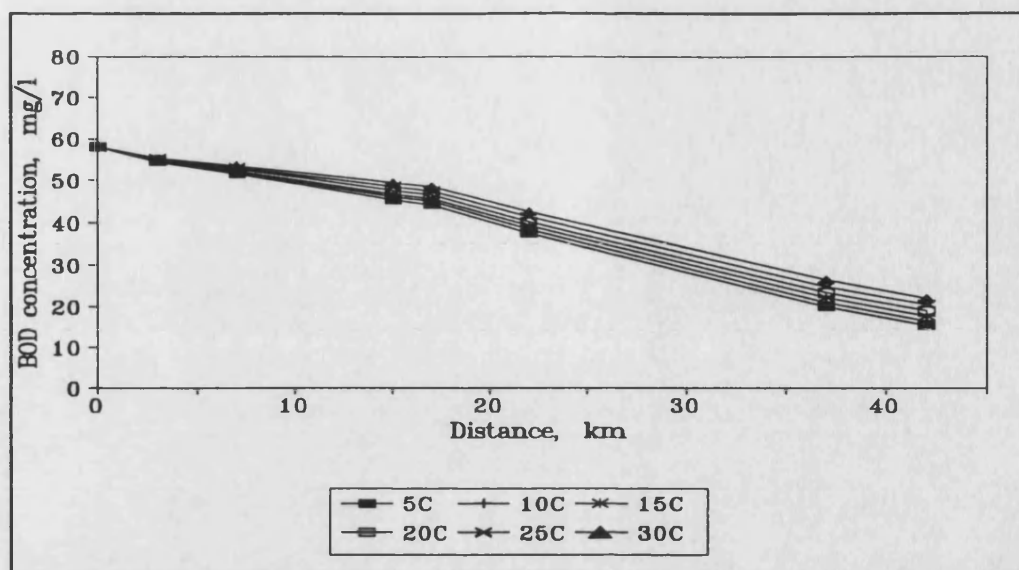


FIGURE 7.7: Biochemical Oxygen Demand (BOD) as affected by temperature change using the Zarka model.

However, bacterial activity is known to increase with temperature over the range found in the Zarka, so consumption of carbonaceous matter is faster at higher temperature. Therefore, the overall temperature effect on BOD is dependent on the state of the water.

As discussed in chapter Five, ammonium decay and nitrate production rates increase with temperature, therefore increasing the temperature of the river from 5°C to 30°C will increase both rates as can be seen from figures (7.8, and 7.9). Ammonium as discussed in chapter five is more affected by physical parameters than nitrate, therefore the temperature effect on nitrate is consistent over the studied range while ammonium is affected more at higher temperatures. The increase in ammonium decay and nitrate production with temperature can be related to the increase in bacterial and algal activities over this range.

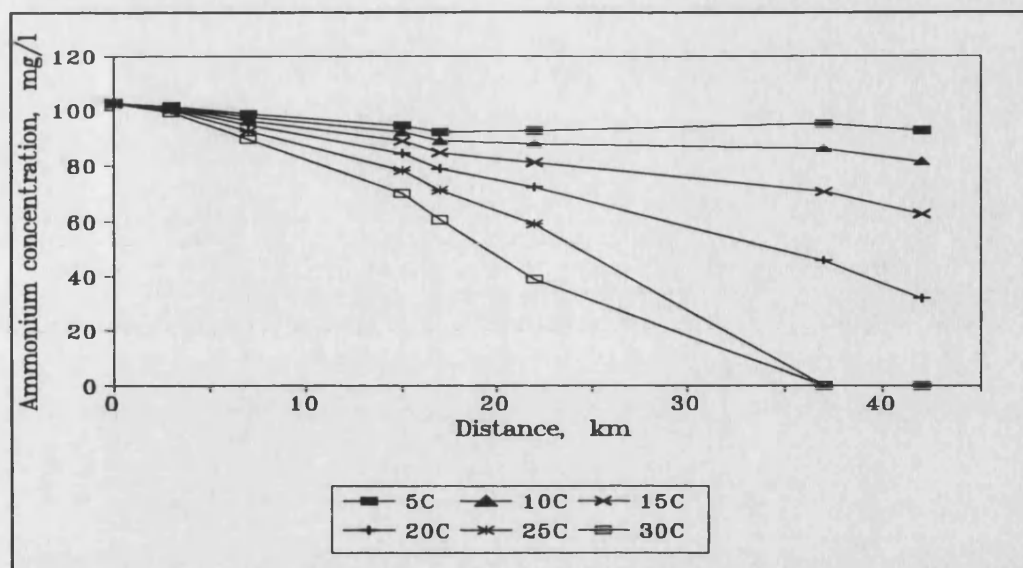


FIGURE 7.8: Ammonium concentration as modelled at different temperatures by the Zarka model.

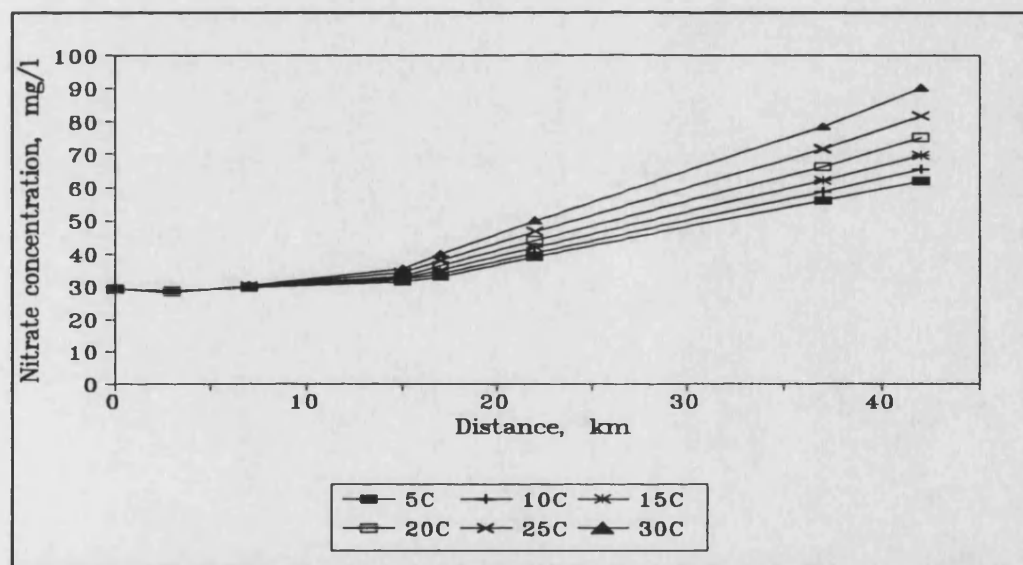


FIGURE 7.9: Nitrate concentration modelled at different temperatures by the Zarka model.

Temperature mostly affects the saturation capacity of the water. It is known that DO saturation increases when temperature decreases. The resulting oxygen behaviour is plotted in figure (7.10) at a wide range in temperatures (5-30°C). This relationship was achieved assuming all other conditions the same, i.e. growth and decay rates of bacteria, algal activity, etc. At higher temperatures, bacterial and algal activities tend

to slow down. The optimum temperature for nitrifiers is in the range 25-30° which resulted in faster ammonium decay, hence oxygen consumed due to ammonium oxidation will be less after the fast depletion of ammonium, and will result in oxygen recovery as can be seen from figure (7.10).

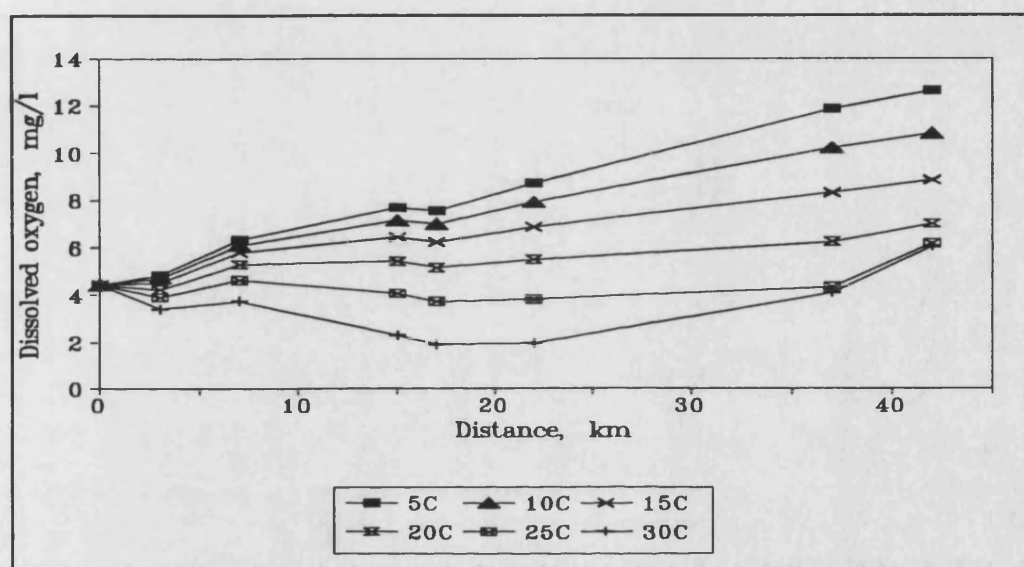


FIGURE 7.10: Dissolved oxygen concentration modelled at different temperatures by the Zarka model.

7.4- EVALUATING THE PREDICTIVE PERFORMANCE OF THE ZARKA MODEL:

The Zarka as a stream highly polluted by high concentrations of organic and inorganic compounds, requires significant improvements in its quality for it to be useful for unrestricted irrigation and possibly recreation. Quality improvements may be achieved by improving the performance of the Waste Stabilization Ponds (WSP) and/or changing conditions along the river. The degree of improvement will be decided by the final purpose of the water.

Therefore, manipulation of the Zarka model should be useful in predicting the effect

of imposing a suggested improvement. The following evaluations were conducted using the model to assess what was needed to achieve two different cases of river quality improvement, (all other conditions were kept the same and the only changed parameters are those mentioned in the evaluations). However, these evaluations were selected to reflect the most desirable river water quality to meet, at least, the Jordanian standards of irrigation water quality. The ultimate aim is to achieve low BOD, low bacterial count, complete nitrification, and high oxygen levels.

EVALUATION ONE:

If BOD concentration is reduced by a factor of 35% at site 2 (WSP outlet), the resulting dissolved oxygen will improve along the river course and reach saturation values after (site 7) and BOD approaches zero at the King Talal Dam (KTD) inlet. While if BOD was reduced by a factor of 65%, the BOD will reach a minimum value faster at (site 7) and DO levels will also rise faster along the river course, reaching saturation after site 5.

EVALUATION TWO:

If ammonium concentration is reduced by a factor of 30% at the WSP outlet, this will result in complete oxidation of ammonium at the KTD inlet. DO levels will increase, as less ammonium is oxidized, but nitrate will not be significantly affected as it depends on the rate of ammonium decay (which was kept the same as only the initial concentration of ammonium was changed). In addition nitrate depends on other factors like bacterial and algal activities, therefore its dependence on ammonium oxidation constitute a small fraction which will not lead to a significant nitrate rise.

EVALUATION THREE:

If the bacterial content is reduced by a factor of 30% by changing the WSP

performance before site 2 (e.g. more settling of bacteria), this theoretically will adversely affect ammonium decay as it decreases with decreasing bacterial activity. But on the other hand, less bacteria means less oxygen demand so more oxygen will be available for ammonium oxidation, therefore ammonium will still be reduced, (depending on the amount of oxygen available). This was predicted by the model which showed that even at lower bacterial content, ammonium will still be oxidized due to more available oxygen. Nitrate will consequently increase due to ammonium oxidation. After the depletion of ammonium and less bacterial demand, oxygen will recover more at down stream sites.

EVALUATION FOUR:

If algal activity is improved by reducing water toxicity and hence the ratio of maximum to minimum oxygen in a diurnal DO increased by a factor of 5%, this will result in complete reduction of ammonium at the KTD inlet. DO levels will increase, but will not be significantly affected by oxidation of ammonium as the amount of oxygen required needed for ammonium oxidation was substituted by the extra amount provided by the increase in algal activity. Nitrate production will also be increased, but to an acceptable level, i.e. 10% higher than the present concentration.

EVALUATION FIVE:

Salinity of the river water affected the DO saturation concentration (which is reflected by higher oxygen deficit), but did not affect the overall DO level, i.e. a reduction of 50% in salinity will only result in 1% increase in DO concentration. This is attributed to salinity constituting only a small fraction of the factors affecting DO level, e.g., bacterial concentration, algal biomass, ammonium oxidation and benthic demand. However, this does not mean that salinity should not be reduced. On the contrary,

salinity must be reduced as it affects the quality of the river water and its suitability for different uses, as well as algal and bacterial activities.

Considering the above evaluations, two hypothetical cases were adopted for improvement of the river water quality with the ultimate purpose to completely reduce ammonium, acceptable nitrate levels, low BOD, and to keep the river well oxygenated, figures (7.11 , 7.12 , 7.13 , and 7.14).

HYPOTHETICAL CASE 1:

- 1- The bacterial concentration is kept the same.
- 2- Increasing the algal activity by decreasing water toxicity and therefore increasing the ratio of maximum to minimum oxygen concentration in a diurnal DO by a factor of 5%.
- 3- Reducing the BOD at the WSP outlet by a factor of 35%.
- 4- All other conditions are to be kept the same, e.g. river velocity, width, sedimentation, etc.

This situation will result in complete reduction of ammonium at the KTD inlet, DO levels will be kept high and approach saturation, BOD will drop to a minimum by KTD inlet, and nitrate will only be raised by 10%, figures (7.11, 7.12, 7.13, and 7.14).

Although this hypothetical case will result in complete reduction of ammonium concentrations by the KTD inlet, initial ammonium levels at upstream sites will still be high enough to be toxic to aquatic life. Therefore, these levels must be reduced to allow fish life and extend the use of the water along the river for unrestricted

irrigation and recreation. This led to hypothetical case 2.

HYPOTHETICAL CASE 2:

- 1- The reduction of the bacterial content is important to both human and plant life, therefore the bacterial concentration is reduced by 30% at the WSP outlet (site 2).
- 2- Ammonium concentration is reduced by 70%, and
- 3- BOD concentration is reduced 30%.
- 4- Algal activity is increased by 5%.

This will lead again to a complete reduction of ammonium, increase the DO levels to approach saturation along the river, and greatly reduce BOD. However, nitrate concentrations, assuming no denitrification is taking place, will consequently increase, (figures 7.11, 7.12, 7.13, and 7.14). This hypothetical case can be achieved by improving the WSP performance by allowing more aeration within the lagoons (especially within the Maturation ponds), to increase nitrification and reduce ammonium to acceptable limits that can be discharged into the river. Higher settling of bacteria and carbonaceous matter will also be needed. Monitoring should be undertaken as denitrification starts to take place after the depletion of ammonium.

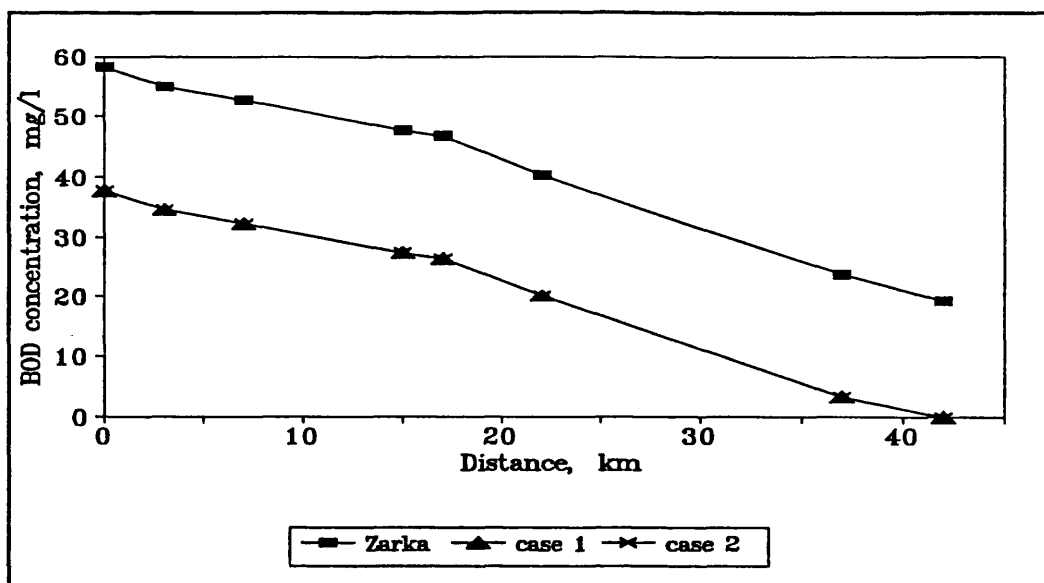


FIGURE 7.11: BOD decay under two hypothetical cases for Zarka water quality improvement.

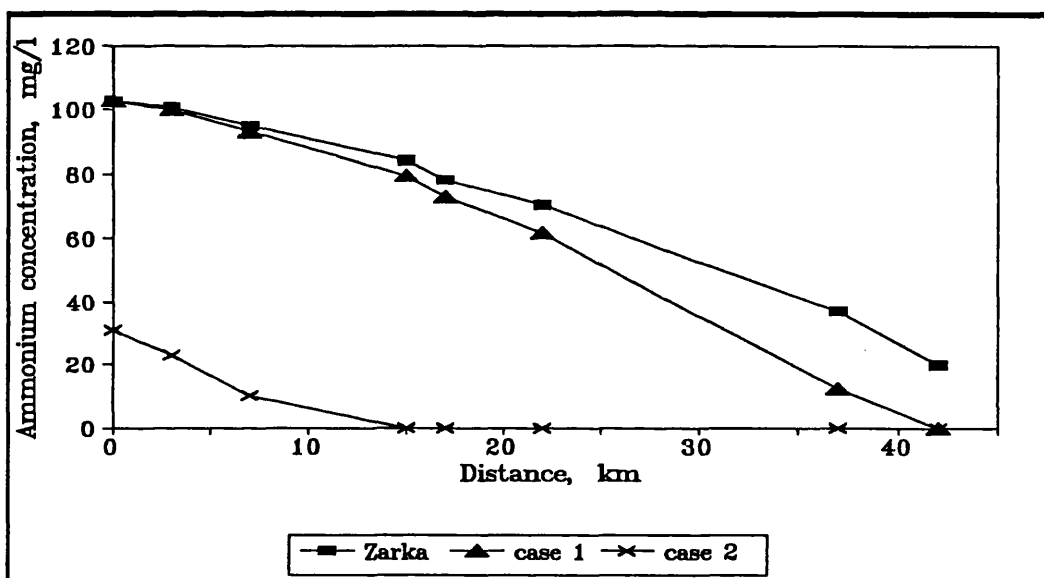


FIGURE 7.12: Ammonium decay under two hypothetical cases for Zarka water quality improvement.

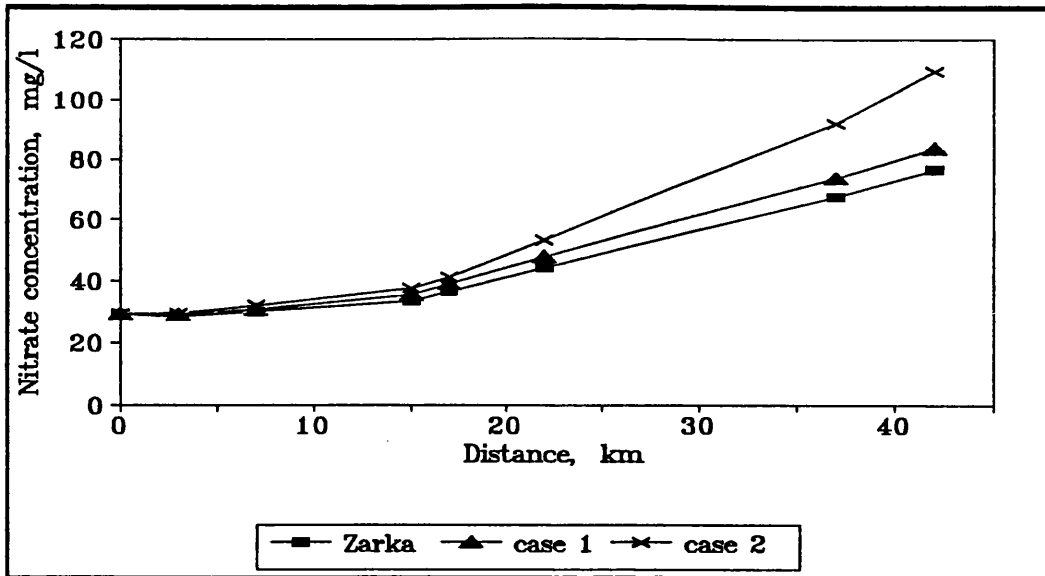


FIGURE 7.13: Nitrate production under two hypothetical cases for Zarka water quality improvement.

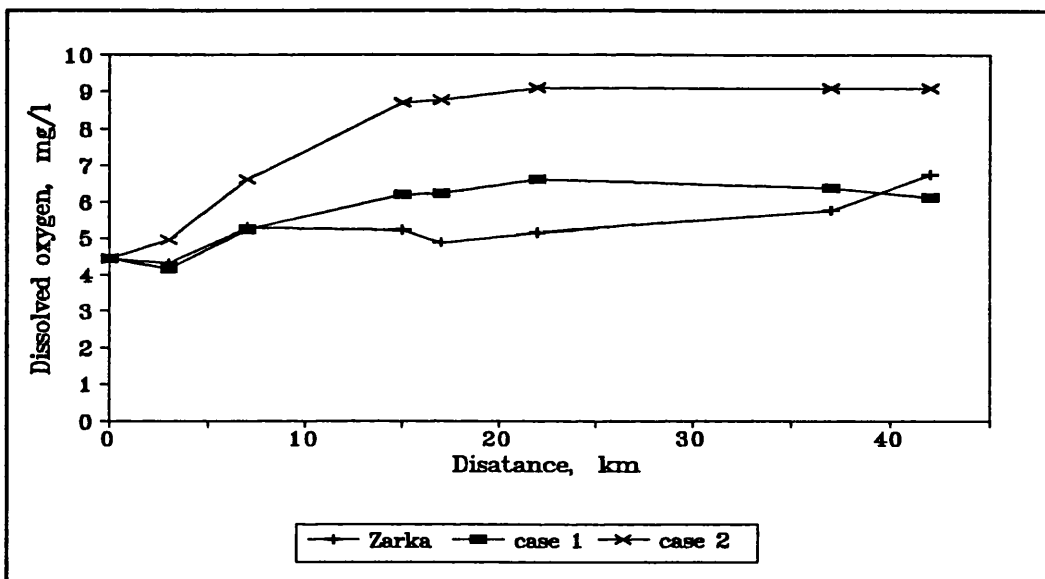


FIGURE 7.14: Dissolved oxygen under two hypothetical cases for water quality improvement of the Zarka.

7.5- CONCLUSIONS:

A river water quality model is presented. The nitrification processes are taken into consideration explicitly in the model. The model is based on three years of water quality analysis and on two comprehensive periods of experimentation to find model parameters. Some basic assumptions were made to simplify the problem and reduce

the number of unknown parameters.

The model is novel in the approach, that algal and bacterial activities are combined to predict river water quality. All reviewed models considered only one of these factors. In addition, algal activity has been expressed in terms of oxygen production rather than algal biomass or chlorophyll concentration. Furthermore, benthic source and demand are expressed in terms of actual sediment quantities per unit area.

The effect of changing several parameters were tested by the model and two hypothetical cases are presented by which river water quality can be improved. However, improvement in river water quality depends largely on improvement of the WSP treatment plant performance, which is the prime source of the river water.

The river is very responsive to environmental changes as it is very shallow (temperature changes by 10°C in a daily cycle). Therefore, the effect of temperature changes was studied by considering a range from 5°C to 30°C. It was found that nitrification, as reduction of ammonium and production of nitrate, increased with temperature, while oxygen concentration was decreased as reaeration and saturation concentrations decreased.

The model can serve as a solid base for any future improvements. Two main issues need further experimental investigations; the effect of river water toxicity and photoinhibition on algal activity, which are considered in this model as correction constants. It is believed that water toxicity along with photoinhibition contribute to

inhibition of complete nitrification. A probable source of toxicity is the heavy metal content of the water as was experienced in 1991, when use of undiluted river water led to an agricultural and economical loss. The main reason was the high concentration of boron discharged by small and medium industrial works (detergents, batteries, sulphochemicals, oil refinery, and others) upstream the treatment plant and the tributary.

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1- INTRODUCTION:

Jordan, a semi-arid country, suffers from a severe shortage of water due to increasing water demand for different domestic, agricultural, and industrial uses. The available water resources in the country, mostly groundwater, are being depleted due to increasing demand, and polluted due to improper use and management.

The government, as well as research centres in the country, are looking for other water resources to substitute some of the country's water needs. Besides water harvesting, and better water management, wastewaters constitute a challenging, but potentially valuable resource, although of course under strictly controlled treatment and reuse.

The River Zarka is the only surface water resource which falls under the sole jurisdiction of the Jordanian government. The river is relatively small but vital and is the only continuous flowing resource during the dry period (which extends eight months a year) feeding the King Talal Dam (KTD). This is the biggest dam in the country and its water is used to irrigate the most fertile part of Jordan.

Over the last few years, the river has received treated, semi-treated and untreated wastewater from the largest wastewater treatment plant of its kind in the Middle East (esSamra Waste Stabilization Ponds), and from other small size treatment plants and refugee camps located either banks of the river. The fresh water wells and springs from which the river used to originate are being withdrawn to fulfil other water needs,

leaving the river with highly polluted water.

The problems associated with the high pollutional state of the river water, necessitates immediate and proper management of the river. This study was started to monitor the water quality of the river, focusing on the transformation of nitrogenous compounds which are contributing to the eutrophication problems of the receiving dam.

Transformation of nitrogenous compounds, commonly known as nitrification and denitrification, are complicated processes involving many influencing factors. Temperature, salinity, acidity, dissolved oxygen, bacterial and algal activities, and high solar radiation are all factors that can affect rates of nitrification and therefore the water quality.

8.2- LITERATURE DISPUTES:

A review of literature on nitrification rates, kinetics and affecting factors showed large discrepancies between reported values for different water systems. Most researchers prefer to express nitrification rate in terms of ammonium decay since nitrate production is more complicated as it involves two stages and more than one type of microorganisms. Some consider the process to be one-stage reaction with the first stage being rate limiting. Differences in nitrification kinetics are due to the nature and conditions surrounding the studied systems, and also the experimental method used can be a substantial factor in affecting the results. However, the kinetics of biological nitrification are not yet thoroughly understood and a number of different rate equations have been derived. As these rate equations lead to a different set of design parameters and stems from different original assumptions, not surprisingly different results have

been produced.

Rates of biochemical oxidation of ammonia and nitrate are naturally unstable and large sampling errors are unavoidable. Many factors determine the rate and extent of nitrogenous oxidation. Variations in rates of nitrogenous oxidation from all sources make it difficult to select appropriate input parameters for computer models that attempt to simulate the natural processes of river self purification.

Therefore, it is concluded that explicit studies are necessary to examine the rate equations of nitrification for rivers, such as the Zarka, which are shallow, polluted and flow through semi-arid regions.

8.3- FACTORS AFFECTING NITRIFICATION IN THE RIVER ZARKA:

Extensive on-site and laboratory tests and experiments have been carried out to determine rates of nitrification in the River Zarka, as affected by the different conditions prevailing in, and surrounding, the river. Another set of experiments have been carried out on an activated sludge effluent to determine points of similarities and disagreements between the two systems.

The experiments carried out on pure culture and river water samples, showed that nitrification was not affected by substrate concentration over the studied range (5-400 mg/l NH_4 and NO_3), which is the range that the Zarka nitrogenous compounds fall within. Moreover, the substrate type, ammonium or nitrate, was also not found to affect nitrification rates.

Different oxygen concentrations were supplied to the activated sludge effluent samples, seeded with River Zarka concentrations of nitrogenous compounds, and this showed that the minimum oxygen concentration necessary for both ammonium decay and nitrate production was between 3-4 mg/l of oxygen which is similar to the value adopted in literature for other river systems. The River Zarka water also needed a minimum concentration of 3-4 mg/l of oxygen for a noticeable ammonium decay, but around 7 mg/l for nitrate production. This indicates that despite the high cell concentration in the River Zarka, the toxicity of the water (and not the substrate concentration), inhibited complete nitrification by increasing oxygen demand and decreasing photosynthetic activity. However, above the minimum level, both systems (the AS effluent and the River Zarka) were affected by the amount of oxygen provided.

The rate of nitrate production, when oxygen was not limited for the AS effluent, was 3-4 times greater than that for the Zarka water. While for ammonium oxidation it was similar. This indicates that the first nitrification stage is not rate limiting, hence nitrification should be considered as a two stage rather than a one stage process. The production of nitrate in the second stage of the process is more complicated, since it depends on the decay of ammonium and involves two types of bacteria (*Nitrosomonas europaea* and *Nitrobacter winogradskyi*), the second of which acts at a slower rate than the first and depends on the presence of *Nitrosomonas europaea*.

At different temperatures, both systems the activated sludge and the Zarka showed the same trends, albeit with different rates, hence the effect of temperature on nitrification

is not significantly affected by the quality of the water. Also, changing cell concentration in both systems had a similar effect on the nitrification trend, although again actual rates were different.

The power law was found to provide good correlation between temperature and nitrification rates. A modified power law was found to best describe the relationship between cell concentration and ammonium decay rate. A Modified Reciprocal Straight line (MRS) model succeeded in simulating nitrate production, but failed to adequately simulate ammonium decay since the latter depends on physical factors such as natural purification through aeration, in addition to dependence on microbial cells.

The chlorophyll content of the Zarka water does not represent the actual algal activity of the river due to chlorination at the treatment plant outlet, toxicity of the water, and photoinhibition from high solar radiation intensities. The photosynthetic activity measured in the river, represents only the freshly produced algae along the course and does not therefore relate to the high chlorophyll concentrations. It was found that the difference between the minimum and maximum oxygen concentrations in a diurnal DO better represents algal activity than did chlorophyll concentration or algal biomass.

The sediment oxygen demand was found to be higher downstream in response to lower down-stream velocities and increased sedimentation. Oxygen consumption due to sediment oxygen demand could not be fully substituted by oxygen produced through the photosynthetic activity of algae.

8.4- APPLICATION OF OTHER WATER QUALITY MODELS:

In the past years considerable effort has been put into the development and application of mathematical models for the prediction of water quality of streams. This effort was to hopefully produce a universal model that could be used on any river or lake, sometimes with calibration, in order to predict quantitatively the consequences of increased pollutional load on water quality, or preferably to indicate how to improve water quality with the implementation of abatement technology. Unfortunately, no such universal model has been successfully developed.

Two well known river water quality models, namely the Blackwater and Qual 2EU models were applied to the River Zarka to assess its water quality in terms of nitrification parameters. Each of these two models uses a different approach in modelling nitrification. The Blackwater model uses bacterial biomass as the key control of nitrification, while the Qual 2EU model uses algal biomass.

Both models, the Blackwater and the Qual 2EU, showed no major discrepancies between measured and simulated concentrations of DO, BOD, NO_3 and NH_4 when simulating the Blackwater and the Winooski rivers, respectively. However, applying the conditions of the River Zarka to both models, (using assumptions made by these models) failed partially or totally to adequately simulate the River Zarka. The prime reason is the nature of the river, being highly polluted with high concentrations of ammonium, high bacterial counts, and a high algal biomass with low activity. Moreover, the River Zarka is a shallow fast flowing river with an average depth of 40 cm, an average velocity of 0.43 m/s and a width ranging between 3-17 meters.

In the River Zarka, both the bacterial and algal biomass were found to be very high. The experimental work carried out with these two factors showed that they are equally important, and both factors must be included in any model to be used in order to predict nitrification in the river.

8.5- THE ZARKA MODEL:

A developed river water quality model is represented. The nitrification processes are taken into consideration explicitly in the model. The model is based on two years of water quality analysis and on two comprehensive periods to find model parameters. Where possible, basic assumptions were made to simplify the problem and reduce the number of unknown parameters.

The novelty of the model stems from the fact that it combines the two major factors affecting nitrification, (i.e. bacterial and algal activity) in a real river system with the conditions of the River Zarka. Although, bacterial and algal biomass activities in nitrification processes have been studied separately by many researchers, they were not combined and applied to a real river system before.

Algal activity is represented in the Zarka model by the ratio of maximum to minimum oxygen concentrations in diurnal DO, rather than by using the algal biomass or chlorophyll concentration which were proved to be misleading in the case of the River Zarka.

In addition, benthic oxygen demand and benthic source of ammonium were expressed in terms of actual sediment loads, rather than a factor which considers the history of

nitrification in waters overlaying sediments as adopted by the Blackwater model.

Moreover, rates of nitrification were experimentally found, both on-site and in the laboratory, and were not assumed prior to modelling as many researchers prefer to do for simplicity.

The effect of changing several parameters are tested by the model to reach two hypothetical cases by which the river water quality would be improved. However, the improvement of the river water quality largely depends on improvement of the performance of the WSP treatment plant which is the prime source of the river water.

The river is highly responsive to environmental changes as it is a shallow river. Temperature can change by 10°C in a daily cycle, Therefore, the effect of temperature changes is studied by considering a range from 5°C to 30°C. It was found that nitrification, as reduction of ammonium and production of nitrate, increased with temperature, while oxygen concentration was decreased as reaeration and saturation concentrations decreased.

8.6- RECOMMENDATIONS FOR FUTURE WORK:

The time and facilities allowed for this study have led to adopting some assumptions to simplify the mathematical side of the model. These assumptions can be tested experimentally to possibly better represent the natural behaviour of assumed parameters. The importance of some factors which arose during the formulation of the model were not expected at the very beginning of this research programme.

The model can serve as a solid base for any future developments. Two main issues are to be taken into consideration; the effect of river water toxicity and photoinhibition on algal activity, which are considered in this model as correction constants. It is believed that the toxicity of the water along with photoinhibition have inhibited complete nitrification. The probable source of toxicity is the heavy metal content of the water as was experienced in 1991 when the use of undiluted river water led to an agricultural loss. The main reason was the high concentrations of boron discharged from small and medium industrial works upstream the treatment plant and the tributary.

More comprehensive and detailed studies are needed on algal activities in terms of oxygen production over a diurnal cycle as well as the seasonal cycle, to better incorporate algal activity in the model, and closer studies on the activity of algae extracted from the river under different conditions of temperature, light intensities and different levels of toxicity.

Nitrifiers were assumed to occupy an equal steady proportions of the total bacterial count. To allow for seasonal changes in numbers of nitrifiers, a detailed study is needed to formulate a factor which can be added to the model to better represent the specific nitrifiers effect, rather than using just a total bacterial count.

The effect of temperature on algal, benthic and bacterial activities may be better represented if these parameters were studied on pure cultures isolated from the river water itself in order to adopt a temperature correction factors that consider daily and

seasonal temperature variations in the river.

Another study can be carried out on the effect of the suspended matter particle size on reaeration by examining different suspended solid loads under different conditions of the river.

The effect of high concentrations of phosphate on algae and on oxygen consumption may be carried out considering the effect of excess nutrients which allow algae to store nutrients until needed.

Diurnal studies on ammonium, nitrate and BOD concentrations are needed to better represent the model findings in terms of light and dark experiments.

APPENDIX A1

TABLE A1.1: Measured and corrected nitrate and ammonium rates of the River Zarka using both Qual 2EU and Zarka correction factors.

Site	Temp. °C	Nitrate production rate (mg/l/min)			Ammonium decay rate (mg/l/min)		
		<i>Measured</i>	<i>Qual 2EU factor (1.047 ± 0.0004)</i>	<i>Zarka factor (1.118 ± 3.4x10⁻⁴)</i>	<i>Measured</i>	<i>Qual 2EU factor (1.047 ± 0.007)</i>	<i>Zarka factor (1.035 ± 3.8x10⁻³)</i>
2	15	0.01	0.02	0.01	0.20	0.23	0.24
	20	0.02	0.02	0.02	0.29	0.29	0.29
	25	0.04	0.03	0.03	0.31	0.36	0.34
5	15	0.02	0.02	0.02	0.36	0.32	0.34
	20	0.03	0.03	0.03	0.40	0.40	0.40
	25	0.04	0.04	0.05	0.48	0.50	0.48
6	15	0.03	0.03	0.02	0.13	0.12	0.13
	20	0.04	0.04	0.04	0.15	0.15	0.15
	25	0.06	0.05	0.07	0.17	0.19	0.18

TABLE A1.2: Measured and corrected nitrate and ammonium rates of the activated sludge effluent using both Qual 2EU and Zarka correction factors.

Ammonium conc. (mg/l)	T °C	Nitrate production rate (mg/l/min)			Ammonium decay rate (mg/l/min)		
		<i>Measured</i>	<i>Qual 2EU factor (1.047 ± 0.111)</i>	<i>Zarka factor (1.118 ± 0.009)</i>	<i>Measured</i>	<i>Qual 2EU factor (1.047 ± 0.003)</i>	<i>Zarka factor (1.035 ± 0.002)</i>
25	15	0.10	0.21	0.15	0.15	0.16	0.17
	20	0.27	0.27	0.27	0.20	0.20	0.20
	25	0.47	0.34	0.47	0.21	0.25	0.24
50	15	0.11	0.20	0.14	0.15	0.14	0.14
	20	0.25	0.25	0.25	0.17	0.17	0.17
	25	0.49	0.31	0.44	0.23	0.21	0.20
100	15	0.12	0.20	0.14	0.15	0.15	0.16
	20	0.25	0.25	0.25	0.19	0.19	0.19
	25	0.48	0.31	0.44	0.22	0.24	0.23
Standard Control (20 mg/l)	15	0.12	0.21	0.15	0.13	0.13	0.13
	20	0.27	0.27	0.27	0.16	0.16	0.16
	25	0.48	0.34	0.47	0.21	0.20	0.19

APPENDIX A2

225a

TABLE A2.1: Site 1 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	7.04	7.01	7.08	6.86	7.03	6.97	7.00
Temp (°C)	19.9	16.2	25.3	24.6	18.1	25.0	22.1
DO (mg/l)	0.57	0.95	0.37	0.52	0.76	0.45	0.56
Redox potential (mV)	1.18	----	0.45	----	0.59	0.22	0.45
NO ₃ (mg/l)	48.2	52.2	32.7	52.4	50.2	42.5	45.7
NO ₂ (mg/l)	0.2	0.4	0.4	0.7	0.3	0.6	0.4
NH ₄ (mg/l)	84.5	94.4	89.4	91.2	89.5	90.3	89.4
PO ₄ (mg/l)	40.6	49.8	44.9	45.3	45.2	45.1	44.6
Cl (mg/l)	365	430	388	392	398	390	390
TOC (mg/l)	202	463	251	276	332	263	280
COD (mg/l)	952	1079	1342	987	1016	1164	1091
BOD (mg/l)	358	357	357	346	358	352	354
Turbidity (ftu)	292	----	146	-----	146	73	121
Chlorophyll. a (µ g/l)	----	----	-----	-----	-----	-----	-----
Nitrobacter *	8x10 ⁶	5x10 ⁷	1x10 ⁷	1x10 ⁷	3x10 ⁷	1x10 ⁷	2x10 ⁷
Nitrosomonas*	1x10 ⁷	8x10 ⁷	1x10 ⁷	1x10 ⁷	4x10 ⁷	1x10 ⁷	2x10 ⁷
Denitrifiers *	1x10 ⁷	7x10 ⁷	2x10 ⁷	2x10 ⁷	4x10 ⁷	2x10 ⁷	3x10 ⁷
HS (mg/l)	2.72	3.48	2.59	2.91	3.10	2.75	2.86
Total Count *	5x10 ⁷	2x10 ⁶	2x10 ⁷	3x10 ⁷	3x10 ⁷	3x10 ⁷	3x10 ⁷
Total Coliform*	3x10 ⁹	1x10 ¹⁰	3x10 ⁹	5x10 ⁹	7x10 ⁹	4x10 ⁹	5x10 ⁹
F. Coliform *	2x10 ⁹ .	6x10 ⁸	3x10 ⁹	6x10 ⁹	1x10 ⁹	4x10 ⁹	3x10 ⁹
Flow rate, m3/s	1.03	1.06	1.14	1.15	1.05	1.15	1.10
Velocity (m/s)	0.65	0.66	0.71	0.72	0.65	0.72	0.69

* (cfu/ml)

TABLE A2.2: Site 2 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.2	7.8	7.8	7.9	8.0	7.8	7.9
Temp (°C)	16.7	11.6	23.5	24.4	14.1	24.0	19.9
DO (mg/l)	3.7	7.8	3.6	3.9	5.8	3.8	4.4
Redox potential (mV)	19.8	--	22.6	--	--	22.6	20.5
NO ₃ (mg/l)	31.3	26.8	24.0	34.1	29.0	29.0	29.3
NO ₂ (mg/l)	0.3	1.2	0.3	0.9	0.8	0.6	0.6
NH ₄ (mg/l)	110.8	98.9	100.4	99.4	104.8	99.9	102.7
PO ₄ (mg/l)	39.5	50.9	45.9	50.8	45.2	48.3	46.3
Cl (mg/l)	358.5	418.8	422.7	405.1	388.7	413.9	399.3
TOC (mg/l)	172.8	320.0	171.2	213.3	246.4	192.3	208.1
COD (mg/l)	312.4	373.9	312.4	278.8	343.2	295.6	313.3
BOD (mg/l)	63.6	37.5	56.3	67.0	50.5	61.7	58.2
Turbidity (ftu)	162.5	--	133.0	--	--	--	146.1
Chlorophyll. a (μ g/l)	469.8	269.7	538.2	497.2	369.7	517.7	463.0
Nitrobacter *	1x10 ⁶	1x10 ⁷	1x10 ⁶	3x10 ⁶	5x10 ⁶	2x10 ⁶	3x10 ⁶
Nitrosomonas*	3x10 ⁶	1x10 ⁷	1x10 ⁶	2x10 ⁶	7x10 ⁶	2x10 ⁶	4x10 ⁶
Denitrifiers *	2x10 ⁶	2x10 ⁷	1x10 ⁶	3x10 ⁶	1x10 ⁷	2x10 ⁶	5x10 ⁶
HS (mg/l)	0.4	0.3	--	0.3	0.3	--	0.3
Total Count *	3x10 ⁶	6x10 ⁶	2x10 ⁶	3x10 ⁶	5x10 ⁶	3x10 ⁶	3x10 ⁶
Total Coliform*	9x10 ⁴	7x10 ²	7x10 ³	4x10 ⁵	4x10 ⁴	2x10 ⁵	1x10 ⁵
F. Coliform *	6x10 ⁴	5x10 ²	6x10 ³	4x10 ⁵	3x10 ⁴	2x10 ⁵	1x10 ⁵
Flow rate, m ³ /s	1.0	1.0	0.9	0.9	1.0	0.9	1.0
Velocity (m/s)	0.4	0.4	0.4	0.4	0.4	0.4	0.4

*(cfu/ml)

TABLE A2.3: Site 3 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	7.9	8.2	7.9	8.0	8.0	8.0
Temp (°C)	16.9	10.9	24.4	24.8	13.9	24.6	19.3
DO (mg/l)	5.9	8.6	4.7	4.6	7.2	4.6	5.8
Redox potential (mV)	21.4	--	21.8	---	21.4	21.8	21.5
NO ₃ (mg/l)	28.3	32.9	15.6	35.1	30.6	25.3	29.8
NO ₂ (mg/l)	1.5	1.3	6.9	5.4	1.4	6.1	3.5
NH ₄ (mg/l)	107.5	99.9	94.6	94.9	103.7	94.7	100.1
PO ₄ (mg/l)	39.3	48.8	32.8	50.3	44.1	41.5	44.0
Cl (mg/l)	343.8	413.0	379.0	409.8	378.4	394.4	384.3
TOC (mg/l)	164.6	227.7	112.7	211.6	196.2	162.2	186.0
COD (mg/l)	304.7	270.1	249.3	251.9	287.4	250.6	272.8
BOD (mg/l)	58.8	31.3	36.3	75.6	45.1	55.9	55.9
Turbidity (ftu)	189.0	---	112.0	---	189.0	112.0	167.0
Chlorophyll. a (μ g/l)	460.4	306.5	863.1	410.4	383.5	636.7	466.7
Nitrobacter *	1x10 ⁷	2x10 ⁷	5x10 ⁶	8x10 ⁶	1x10 ⁷	6x10 ⁶	1x10 ⁷
Nitrosomonas*	1x10 ⁷	3x10 ⁶	6x10 ⁶	9x10 ⁶	7x10 ⁶	8x10 ⁶	8x10 ⁶
Denitrifiers *	1x10 ⁷	1x10 ⁷	4x10 ⁶	6x10 ⁶	1x10 ⁷	5x10 ⁶	9x10 ⁶
HS (mg/l)	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Total Count *	1x10 ⁷	8x10 ⁶	4x10 ⁶	8x10 ⁶	9x10 ⁶	6x10 ⁶	8x10 ⁶
Total Coliform*	2x10 ⁴	2x10 ⁴	4x10 ³	2x10 ³	2x10 ⁴	3x10 ³	1x10 ⁴
F. Coliform *	1x10 ⁴	6x10 ³	2x10 ³	2x10 ³	1x10 ⁴	2x10 ³	7x10 ³
Flow rate, m ³ /s	1.0	1.0	0.9	0.9	1.0	0.9	1.0
Velocity (m/s)	0.4	0.4	0.4	0.4	0.4	0.4	0.4

* (cfu/ml)

TABLE A2.4: Site 4 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	8.0	8.4	8.0	8.0	8.2	8.1
Temp (°C)	17.4	11.9	25.0	25.4	14.7	25.2	20.0
DO (mg/l)	4.4	5.5	3.9	2.8	4.9	3.4	4.0
Redox potential (mV)	21.2	---	22.0	---	21.2	22.0	21.4
NO ₃ (mg/l)	31.0	33.6	19.0	38.8	32.3	28.9	32.5
NO ₂ (mg/l)	2.3	2.3	10.4	6.9	2.3	8.6	4.9
NH ₄ (mg/l)	105.4	101.4	81.1	87.8	103.4	84.4	95.5
PO ₄ (mg/l)	35.7	43.9	31.0	44.4	39.8	37.7	39.6
Cl (mg/l)	360.1	415.2	391.0	412.4	387.7	401.7	392.7
TOC (mg/l)	166.0	206.2	106.5	201.4	186.1	154.0	177.9
COD (mg/l)	297.3	241.8	224.2	236.9	269.6	230.6	256.3
BOD (mg/l)	49.4	35.0	80.0	62.0	42.2	71.0	54.8
Turbidity (ftu)	220.0	---	110.0		220.0	110.0	188.6
Chlorophyll. a (μ g/l)	521.3	161.7	674.3	338.7	341.5	506.5	408.9
Nitrobacter *	1x10 ⁷	8x10 ⁶	4x10 ⁶	3x10 ⁶	1x10 ⁷	3x10 ⁶	7x10 ⁶
Nitrosomonas*	2x10 ⁷	1x10 ⁷	3x10 ⁶	3x10 ⁶	1x10 ⁷	3x10 ⁶	1x10 ⁷
Denitrifiers *	2x10 ⁷	9x10 ⁶	3x10 ⁶	5x10 ⁶	1x10 ⁷	4x10 ⁶	1x10 ⁷
HS (mg/l)	0.3	0.1	0.3	0.2	0.2	0.2	0.2
Total Count *	1x10 ⁷	9x10 ⁶	4x10 ⁶	4x10 ⁶	9x10 ⁶	4x10 ⁶	7x10 ⁶
Total Coliform*	1x10 ⁴	1x10 ⁴	3x10 ³	4x10 ³	1x10 ⁴	4x10 ³	8x10 ³
F. Coliform *	8x10 ³	1x10 ⁴	3x10 ³	3x10 ³	9x10 ³	3x10 ³	6x10 ³
Flow rate, m3/s	1.0	1.0	0.9	0.9	1.0	0.9	1.0
Velocity (m/s)	0.5	0.5	0.5	0.5	0.5	0.5	0.5

* (cfu/ml)

TABLE A2.5: Site 5 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	8.0	8.0	7.9	8.0	8.0	8.0
Temp (°C)	18.1	11.5	24.9	25.4	14.8	25.2	20.9
DO (mg/l)	5.1	5.1	4.1	3.3	5.1	3.7	4.4
Redox potential (mV)	21.1	---	22.4	---	21.1	22.4	21.4
NO ₃ (mg/l)	30.2	34.6	25.0	35.8	32.4	30.4	31.0
NO ₂ (mg/l)	4.1	4.0	12.2	10.9	4.0	11.5	8.2
NH ₄ (mg/l)	103.2	95.6	110.8	87.0	99.4	98.9	99.6
PO ₄ (mg/l)	30.9	43.8	39.6	44.8	37.4	42.2	39.3
Cl (mg/l)	380.0	409.8	402.2	412.3	394.9	407.2	400.1
TOC (mg/l)	166.2	222.7	158.5	185.3	194.4	171.9	178.8
COD (mg/l)	281.3	242.2	224.7	201.8	261.8	213.2	237.0
BOD (mg/l)	45.7	30.7	58.4	55.6	38.2	57.0	49.5
Turbidity (ftu)	205.6	---	96.8	---	205.6	96.8	151.2
Chlorophyll. a (μ g/l)	372.8	309.7	416.8	465.4	341.3	441.1	400.2
Nitrobacter *	9x10 ⁶	6x10 ⁶	2x10 ⁷	3x10 ⁶	7x10 ⁶	1x10 ⁷	1x10 ⁷
Nitrosomonas*	1x10 ⁷	1x10 ⁷	2x10 ⁷	3x10 ⁶	1x10 ⁷	1x10 ⁷	1x10 ⁷
Denitrifiers *	1x10 ⁷	1x10 ⁷	2x10 ⁷	2x10 ⁶	1x10 ⁷	1x10 ⁷	1x10 ⁷
HS (mg/l)	0.3	0.1	0.3	0.2	0.2	0.2	0.2
Total Count *	3x10 ⁷	2x10 ⁷	2x10 ⁷	8x10 ⁶	2x10 ⁷	1x10 ⁷	2x10 ⁷
Total Coliform*	4x10 ⁴	3x10 ³	1x10 ⁴	7x10 ³	2x10 ⁴	1x10 ⁴	2x10 ⁴
F. Coliform *	2x10 ⁴	3x10 ³	1x10 ⁴	6x10 ³	1x10 ⁴	9x10 ³	1x10 ⁴
Flow rate, m3/s	1.0	1.0	0.9	0.9	1.0	0.9	1.0
Velocity (m/s)	0.4	0.5	0.4	0.4	0.4	0.4	0.4

* (cfu/ml)

TABLE A2.6: Site 6 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	7.9	8.0	7.9	7.8	8.0	7.8	7.9
Temp (°C)	18.8	11.5	25.8	26.1	15.2	26.0	21.6
DO (mg/l)	5.5	8.9	5.3	3.3	7.2	4.3	5.4
Redox potential (mV)	20.7	---	21.9	---	20.7	21.9	21.0
NO ₃ (mg/l)	33.7	38.3	24.3	39.0	36.0	31.6	33.3
NO ₂ (mg/l)	5.0	4.1	17.1	12.7	4.6	14.9	10.4
NH ₄ (mg/l)	81.6	69.5	95.4	79.4	75.5	87.4	82.8
PO ₄ (mg/l)	23.2	34.1	32.6	35.2	28.7	33.9	31.0
Cl (mg/l)	386.6	407.8	408.5	422.4	397.2	415.4	406.2
TOC (mg/l)	153.5	114.3	98.5	168.3	133.9	133.4	135.8
COD (mg/l)	223.8	141.6	183.1	195.2	182.7	189.2	190.9
BOD (mg/l)	43.5	25.9	53.4	53.4	34.7	53.4	46.1
Turbidity (ftu)	169.6	----	8.6	0.0	169.6	4.3	82.8
Chlorophyll. a (µ g/l)	460.2	242.9	495.9	448.5	351.6	472.2	430.7
Nitrobacter *	1x10 ⁷	3x10 ⁶	7x10 ⁶	3x10 ⁶	6x10 ⁶	5x10 ⁶	6x10 ⁶
Nitrosomonas*	9x10 ⁶	6x10 ⁶	4x10 ⁶	2x10 ⁶	7x10 ⁶	3x10 ⁶	5x10 ⁶
Denitrifiers *	1x10 ⁷	2x10 ⁶	8x10 ⁶	3x10 ⁶	8x10 ⁶	6x10 ⁶	7x10 ⁶
HS (mg/l)	0.2	0.0	0.2	0.1	0.1	0.1	0.1
Total Count *	1x10 ⁷	7x10 ⁶	1x10 ⁷	5x10 ⁶	9x10 ⁶	8x10 ⁶	9x10 ⁶
Total Coliform*	3x10 ⁴	3x10 ⁴	3x10 ⁴	7x10 ³	3x10 ⁴	2x10 ⁴	3x10 ⁴
F. Coliform *	8x10 ³	7x10 ²	2x10 ⁴	5x10 ³	5x10 ³	2x10 ⁴	1x10 ⁴
Flow rate, m3/s	1.4	3.0	1.3	1.2	2.2	1.2	1.6
Velocity (m/s)	0.6	1.2	0.5	0.5	0.9	0.5	0.6

* (cfu/ml)

TABLE A2.7: Site 7 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	8.1	7.9	7.6	8.1	7.8	7.9
Temp (°C)	20.1	12.1	26.9	26.4	16.1	26.6	21.1
DO (mg/l)	5.5	9.5	4.4	5.2	7.5	4.8	6.1
Redox potential (mV)	20.6	---	21.8	---	20.6	21.8	20.9
NO ₃ (mg/l)	47.9	41.7	37.8	59.8	44.8	48.8	50.1
NO ₂ (mg/l)	5.2	2.8	15.7	19.2	4.0	17.4	10.4
NH ₄ (mg/l)	62.5	50.1	42.5	49.6	56.3	46.1	53.8
PO ₄ (mg/l)	16.3	38.1	30.4	32.1	27.2	31.2	27.6
Cl (mg/l)	380.7	409.4	377.0	423.6	395.1	400.3	401.9
TOC (mg/l)	132.2	93.3	50.8	132.2	112.8	91.5	118.0
COD (mg/l)	161.8	110.7	135.2	167.6	136.2	151.4	151.0
BOD (mg/l)	33.7	12.0	61.0	46.2	22.9	53.6	35.5
Turbidity (ftu)	133.6	---	36.0	----	133.6	36.0	117.3
Chlorophyll. a (μ g/l)	289.7	226.1	289.0	279.1	257.9	284.1	272.3
Nitrobacter *	1x10 ⁶	3x10 ⁶	3x10 ⁶	2x10 ⁶	2x10 ⁶	3x10 ⁶	2x10 ⁶
Nitrosomonas*	2x10 ⁶	4x10 ⁶	3x10 ⁶	3x10 ⁶	3x10 ⁶	3x10 ⁶	3x10 ⁶
Denitrifiers *	4x10 ⁶	2x10 ⁶	2x10 ⁶	2x10 ⁶	3x10 ⁶	2x10 ⁶	3x10 ⁶
HS (mg/l)	0.1	0.1	0.2	0.1	0.1	0.1	0.1
Total Count *	5x10 ⁶	2x10 ⁶	6x10 ⁵	1x10 ⁶	4x10 ⁶	8x10 ⁵	3x10 ⁶
Total Coliform*	1x10 ⁴	1x10 ⁴	8x10 ²	6x10 ³	1x10 ⁴	3x10 ³	8x10 ³
F. Coliform *	8x10 ³	9x10 ³	7x10 ²	5x10 ³	9x10 ³	3x10 ³	7x10 ³
Flow rate, m3/s	1.3	3.0	1.7	1.2	2.2	1.4	1.7
Velocity (m/s)	0.3	0.6	0.3	0.2	0.4	0.3	0.3

* (cfu/ml)

TABLE A2.8: Site 8 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	8.0	8.3	7.7	8.0	8.0	7.9
Temp (°C)	19.1	11.8	27.3	25.9	15.5	26.6	21.0
DO (mg/l)	6.4	9.4	5.8	5.5	7.9	5.6	6.6
Redox potential (mV)	20.7	---	22.1	---	20.7	22.1	21.0
NO ₃ (mg/l)	60.6	45.3	65.6	85.3	52.9	75.5	66.4
NO ₂ (mg/l)	5.8	1.9	7.4	13.1	3.8	10.3	7.7
NH ₄ (mg/l)	40.2	31.8	20.8	21.5	36.0	21.1	29.7
PO ₄ (mg/l)	13.7	26.2	28.1	28.0	19.9	28.1	22.9
Cl (mg/l)	356.7	409.3	393.9	437.9	383.0	415.9	399.2
TOC (mg/l)	85.7	61.1	65.7	73.4	73.4	69.6	74.0
COD (mg/l)	107.2	80.7	121.5	110.5	94.0	116.0	104.9
BOD (mg/l)	25.1	8.3	47.5	34.8	16.7	41.2	28.0
Turbidity (ftu)	84.3	---	23.0	---	84.3	23.0	63.8
Chlorophyll. a (μ g/l)	194.7	158.5	214.4	72.6	176.6	143.5	149.4
Nitrobacter *	1x10 ⁶	2x10 ⁶	9x10 ⁵	3x10 ⁶	2x10 ⁶	2x10 ⁶	2x10 ⁶
Nitrosomonas*	2x10 ⁶	3x10 ⁶	5x10 ⁵	2x10 ⁶	3x10 ⁶	1x10 ⁶	2x10 ⁶
Denitrifiers *	1x10 ⁶	2x10 ⁶	5x10 ⁵	2x10 ⁶	1x10 ⁶	1x10 ⁶	1x10 ⁶
HS (mg/l)	0.1	0.0	0.1	0.1	0.1	0.1	0.1
Total Count *	2x10 ⁶	2x10 ⁶	4x10 ⁵	1x10 ⁶	2x10 ⁶	7x10 ⁵	1x10 ⁶
Total Coliform*	3x10 ⁴	2x10 ³	8x10 ³	7x10 ³	2x10 ⁴	7x10 ³	2x10 ⁴
F. Coliform *	3x10 ⁴	2x10 ³	7x10 ³	5x10 ³	1x10 ⁴	6x10 ³	1x10 ⁴
Flow rate, m ³ /s	1.4	3.0	1.4	1.2	2.2	1.3	1.7
Velocity (m/s)	0.3	0.7	0.3	0.3	0.5	0.3	0.4

* (cfu/ml)

TABLE A2.9: Site 9 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.0	8.0	7.9	7.7	8.0	7.8	7.9
Temp (°C)	19.1	11.2	26.1	26.5	15.2	26.3	21.8
DO (mg/l)	6.2	10.6	6.9	5.5	8.4	6.2	6.9
Redox potential (mV)	21.9	---	21.0	---	21.9	21.0	21.7
NO ₃ (mg/l)	63.8	48.2	88.6	94.3	56.0	91.4	76.5
NO ₂ (mg/l)	6.2	1.6	6.3	14.4	3.9	10.4	7.7
NH ₄ (mg/l)	32.4	25.3	21.3	12.2	28.9	16.8	22.5
PO ₄ (mg/l)	16.7	19.4	21.9	20.2	18.0	21.1	19.6
Cl (mg/l)	379.2	441.0	419.7	437.6	410.1	428.7	417.0
TOC (mg/l)	64.3	62.0	45.8	71.3	63.2	58.6	60.7
COD (mg/l)	99.1	71.4	86.3	95.9	85.2	91.1	90.0
BOD (mg/l)	14.0	4.0	19.9	27.3	9.0	23.6	17.7
Turbidity (ftu)	34.0	---	34.9	---	34.0	34.9	34.5
Chlorophyll. a (μ g/l)	127.8	82.1	228.1	68.2	104.9	148.1	131.5
Nitrobacter *	1x10 ⁶	1x10 ⁶	3x10 ⁵	2x10 ⁵	1x10 ⁶	3x10 ⁵	6x10 ⁵
Nitrosomonas*	6x10 ⁵	1x10 ⁶	4x10 ⁵	2x10 ⁵	8x10 ⁵	3x10 ⁵	5x10 ⁵
Denitrifiers *	5x10 ⁵	5x10 ⁵	3x10 ⁵	1x10 ⁵	5x10 ⁵	2x10 ⁵	3x10 ⁵
HS (mg/l)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Count *	6x10 ⁵	5x10 ⁵	3x10 ⁵	2x10 ⁵	6x10 ⁵	2x10 ⁵	4x10 ⁵
Total Coliform*	8x10 ³	7x10 ³	6x10 ³	1x10 ³	8x10 ³	4x10 ³	5x10 ³
F. Coliform *	7x10 ³	4x10 ³	5x10 ³	1x10 ³	6x10 ³	3x10 ³	4x10 ³
Flow rate, m ³ /s	1.3	3.0	1.3	1.2	2.2	1.2	1.6
Velocity (m/s)	0.4	0.9	0.4	0.4	0.7	0.4	0.5

* (cfu/ml)

TABLE A2.10: Site 10 average winter and summer values of all tested parameters.

PARAMETER	winter 90/91	winter 91/92	summer 90/91	summer 91/92	winter average	summer average	Total average
pH-value	8.1	8.1	8.2	8.0	8.1	8.1	8.1
Temp (°C)	20.0	12.2	25.3	25.9	16.1	25.6	21.5
DO (mg/l)	10.9	10.1	9.4	10.6	10.5	10.0	10.4
Redox potential (mV)	21.3	---	22.7	---	21.3	22.7	21.3
NO ₃ (mg/l)	63.3	32.2	56.0	48.6	47.7	52.3	54.1
NO ₂ (mg/l)	0.1	1.7	0.1	0.1	0.9	0.1	0.3
NH ₄ (mg/l)	0.0	3.6	0.0	0.0	1.8	0.0	0.4
PO ₄ (mg/l)	0.2	0.2	0.3	0.3	0.2	0.3	0.3
Cl (mg/l)	534.5	588.7	569.2	559.0	561.6	564.1	560.7
TOC (mg/l)	9.3	33.7	5.6	21.9	21.5	13.8	16.3
COD (mg/l)	22.8	44.2	15.9	29.8	33.5	22.9	27.3
BOD (mg/l)	4.1	4.0	10.5	4.6	4.1	7.6	6.0
Turbidity (ftu)	0.8	---	0.7	---	0.8	0.7	0.6
Chlorophyll. a (μ g/l)	7.9	4.7	7.1	6.2	6.3	6.7	6.8
Nitrobacter *	1x10 ⁵	2x10 ⁵	6x10 ⁴	3x10 ⁵	1x10 ⁵	2x10 ⁵	2x10 ⁵
Nitrosomonas*	1x10 ⁵	2x10 ⁵	3x10 ⁴	2x10 ⁵	2x10 ⁵	1x10 ⁵	1x10 ⁵
Denitrifiers *	2x10 ⁵	3x10 ⁵	2x10 ⁴	3x10 ⁵	2x10 ⁵	2x10 ⁵	2x10 ⁵
HS (mg/l)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Count *	2x10 ⁵	1x10 ⁵	1x10 ⁴	3x10 ⁵	2x10 ⁵	2x10 ⁵	2x10 ⁵
Total Coliform*	4x10 ²	1x10 ³	3x10 ²	6x10 ²	8x10 ²	4x10 ²	5x10 ²
F. Coliform *	4x10 ²	1x10 ³	2x10 ²	3x10 ²	8x10 ²	3x10 ²	4x10 ²
Flow rate, m3/s	0.5	0.9	0.3	0.2	0.7	0.3	0.4
Velocity (m/s)	0.5	0.9	0.3	0.2	0.7	0.3	0.4

* (cfu/ml)

APPENDIX A3

TABLE A3.1: Listing of the mathematical construction used in the simulation of the Zarka model by a Quattro Pro for Windows spreadsheet.

1	Parameter (Cell A)	Inlet to reach one (Cell B)	Outlet of reach one (Cell C)
2	Depth, m	0.65	0.65
3	Distance, km	0.00	3.00
4	Temperature, °C	19.90	19.30
5	DO mg l^{-1}	4.43	5.83
6	NO_3 mg l^{-1}	29.27	29.79
7	NO_2 mg l^{-1}	0.61	3.47
8	NH_4 mg l^{-1}	102.74	100.05
9	Cl mg l^{-1}	399.34	384.33
10	BOD mg l^{-1}	58.17	55.91
11	Total Count, cfum l^{-1}	3.3×10^6	8.1×10^6
12	Velocity, ms^{-1}	0.37	0.37
13	$f = L/\text{BOD}$ measured	1.186	1.181
14	L (uBOD), mg l^{-1}	68.99	$((C13)*(C10))$
15	travel time min	0.00	134.23
16	TSS mg l^{-1}	1270.00	1366.00
17	Salinity ppt	0.75	$(0.03 + (0.00181*(C9)))$
18	weight of sediment kg km^{-2}	3536.78	3678.25
19	River width km	0.004	0.005
20	Area km^2	0.00	$((C3)*(C19))$
21			
22	DO_s	9.00	$14.62 - (0.37*(C4)) + (0.0045*((C4)^2))$ $-(0.097*(C17)) + (0.0021*(C17)*(C4))$ $+(0.0003*((C17)^2))$

TABLE A3.1: Continue

23	DO deficit	4.57	$((C22)-(C5))$
24	k_2 reaeration	0.00	$(@LN(B23)-@LN(C23))/(C15)$
25	Scott's factor	0.00	$1.063-(0.256*(@LOG(C16)))$
26	k_2 corrected	0.00	$((C24)*(C25))$
26	due reaeration at T °C	0.00	$(C26)*((C22)-(C5))$
28	k_1 BOD measured.min ⁻¹	0.00	3×10^{-4}
29	k_1 at T °C	0.00	$(C28)*(1.016^{((C4)-20)})$
30	BOD model:		
31	due BOD decay	0.00	$((C29)*(C14))$
32	Due to BOD resuspension	0	$(k_3)*(C14)$
33	simulated dBOD/dt	0.00	$((-C31)+(C32))$
34	BOD simulated	58.17	$((B34)-((C33)*(C15)))$
35	DO model		
36	$k_1*(BOD)$	0.00	$((C29)*(C34)*(C13))$
37	oxygenation rate (measured)	0.00	r_5
38	due to light and photosynthesis		
39	AT T °C	0.00	$((1.061^{((C4)-20)})*(\alpha_5)*(C37)*(C72))$
40	due to sediment		
41	deoxygenation due sediment (measured)	0.01	r_6
42	AT T °C	0.00	$(\alpha_4)*(C20)*(C18)*(C41)$

TABLE A3.1: Continue

43	due to ammonium		
44	AT T °C	0.00	$1.047^{((C4)-20)} * 4.33 * (r_7) * (B57)$
45	dDO/dt	0	$(C27) - (C36) + (C39) - (C42) - (C44)$
46	DO simulated	4.43	$((B46) - ((C45) * (C15)))$
47	NH ₄ model		
48	due to bacteria		
49	AT T °C	0.00	$(1.047^{((C4)-20)} * ((0.18 * ((C11)^{0.017}) - 0.17))$
50	due to algae		
51	AT T °C	0.00	$(1.047^{((C4)-20)} * ((r_1) * (C72)))$
52	due to sediment		
53	AT T C	0.00	$((r_3) * ((C18) * (C20)))$
54	NH ₄ oxidation rate coefficient min ⁻¹	0.00028	0.00029
55	Due to NH ₄ oxidation	0	$1.047^{((C4)-20)} * (C54) * (C57)$
56	dNH ₄ /dt simulated	0.00	$(-(C49) + (C51) - (C53) - (C55))$
57	NH ₄ simulated	102.74	$((B57) - ((C56) * (C15)))$
58			
59	NO ₃		
60	due to bacteria		
61	AT T °C	0.06	$1.047^{((C4)-(20))} * (((0.065 * (1.1E-05 * (C11))) / ((0.065 + (1.1E-05 * (C11))))))$
62	due to algae		
63	AT T °C	0.06	$1.047^{((C4)-20)} * ((r_2) * (C72))$
64	NO ₃ prod rate	6.8×10^{-4}	6.7×10^{-4}

TABLE A.3.1: Continue

65	due to NH ₄ oxidation		
66	AT T °C	0.00	$1.047^{((B4)-20)} * 0.98 * (C64) * ((B57)-(C57)) / (C15)$
67	due to sediment		
68	AT T °C	0.00	$((r_4) * (C18) * (C20))$
69	dNO ₃ /dt	0.00	$((C61)-(C63) + (C66)-(C68))$
70	NO ₃ simulated	29.27	$(B69) - ((C69) * (C15))$
71	NO ₃ measured	29.27	29.79
72	Ratio (R) max/min DO	1.18	1.25

Coefficients and constants are found in table (7.2), chapter seven.

BIBLIOGRAPHY

Abumoghli I and Ghuneim N., (1990). Manual of water analyses. Bulletin of the Water Research and Study Centre, University of Jordan, University press.

Abumoghli I, (1991 and 1992). Eutrophication in King Talal Dam. Unpublished data.

Al-Layla M. Anis and Al-Rizzo M. Hasan., (1989). A water quality model for the Tigris River downstream of Saddam Dam, Iraq. Journal of Hydrological Sciences, Vol.34, No.6.

Alford J. A., (1969). Effect of incubation temperature on biochemical tests in the genera *Pseudomonas* and *Achromobacter*. Journal of Bacteriology. 79, 591-593.

Arceivala S. J. (1981). Wastewater treatment and disposal, Engineering and Ecology in Pollution Control", Marcel Dekker, Inc.

Barber J. (1987), (editor). Photoinhibition; Topics in photosynthesis. Vol.9, chapter 2. Elsevier. Oxford.

Barnwell T. O. (1983). Stormwater and water quality model users group meeting-proceedings held on January 27-28, 1983. EPA 600/0-83-015. J Environmental Research Lab., Athens, GA.

Beccardi M., Pinto A. C., Ramadori R. and Tomei M. C., (1984). Effects of dissolved oxygen and diffusion resistances on nitrification kinetics. Wat. Res. Vol. 26. No. 8. pp 1099-1104.

Bergey's manual of systematic bacteriology. (1984). Edited by Krieg N. R. and Holt J. G. Williams and Wilkins. Vol. 1.

Bergey's manual of determinative bacteriology. (1974). Edited by Buchanan R. E and Gibbons N. E. Williams and Wilkins. 8th ed.

Billen Gills. (1975). Nitrification in the Scheldt Estuary (Belgium and the

Netherlands). *Estuary and Coastal Marine Science*. 3, 79-89.

Bino Murad J. (1990). Urbanization and industrialization impacts on water reservoir; A case study: King Talal Reservoir. Presented at the Second Environmental Pollution Symposium. Water Pollution- Causes and Effects. Amman. University of Jordan.

Borland international (1992). Quattro Pro for Windows. version 1.00. School of Chemical Engineering, University of Bath.

Brown L. C. et al. (1987). Enhanced stream water quality models Qual 2E and Qual 2E-UNCAS: Documentation and user manual. EPA/600/3-87/007. (EPA), US Environmental Protection Agency. Athens, GA.

Canter L. W. (1988). Water pollution impacts. Lecture presented at the 5th International Advanced Course on Water Resources Management, Water for Health, Water for Food, Water for Energy. WARREDOC, Italy.

Carpenter Edward J. and Capone Douglas G. (1983). Nitrogen in the marine environment. Academic Press.

Casapieri P., Fox T. M., Owers P. and Thomson G. D. (1978). A mathematical deterministic river quality model. Part 2: Use in evaluating the water quality management of the Blackwater catchment. *Water Research*. 12, 115-1161.

Chen Carl W. and Wells Jhon T. J. (1975). Biose River ecological modelling. Tetra Tech. Tnc., Lafayette, California.

Chesterikoff A. Garban B. and Ollivon D. (1991). Daily rhythms in the river Seine: Relative impacts of natural and anthropogenic factors. *Wat. Res.* Vol. 25. No. 12. pp 1523-1528.

Cooper Bryce A. (1986). Developing management guidelines for River nitrogenous oxygen demand. *J. Water Pollut. Control Fed.* 58(8), 845-52.

- Courchaine** Robert J. (1962). Significance of nitrification in stream analysis - Effect on the oxygen balance-. Paper Presented at the 37th Annual Conference of the Michigan Water Pollution Control Association, Traverse City, Mich.
- Crabtree** R. W., Cluckie I. D., Forster C. F. and Crockett C. P. (1986). A comparison of two river quality models. *Water Resources*. Vol. 20. No 1. pp 53-61.
- Curtis** E. J., Durrant K. and Harman M. M. (1975). Nitrification in rivers in the Trent basin. *Wat. Research*. Vol. 9. pp 255-268.
- Dodd** D. J. R. and Bone D. H. (1975). Nitrate reduction by denitrifying bacteria in single and two stage continuous flow reactors. *Water Research* 9, 323-328.
- Dunnette** David A. and Avedovech Richard M. (1983). Effect of an industrial ammonia discharge on the dissolved oxygen regime of Willamette River, Oregon. *Water Res.* Vol. 17, No. 9 pp. 997-1007.
- Eckenfelder** Wesley W., J. (1989). *Industrial water pollution control*. 2nd Edition, McGraw Hill.
- Fair** G. M., Geyer J. C. and Okun D. A. (1971). *Elements of water supply and wastewater disposal*. Jhon Willy & Sons, 2nd Ed.
- Garnier** J., Servais P. and Billen G. (1992). Bacterioplankton in the Seine River(France): impact of the Parisian urban effluent. *Ca. J. Microbiol.* 38: 56-64.
- Gee Chai Sung**, Pfeffer J. T. and Suidan M. T. (1990). Nitrosomonas and Nitrobacter Interactions in Biological Nitrification", *Journal of Environmental Engineering*. 1(116), 4-17.
- Gee Chai Sung**, Pfeffer J. T. and Suidan M. T. (1990). Modelling of nitrification under substrate-inhibiting conditions, *Journal of Environmental Engineering*, Vol. 1(116), 18-31.

- Grant W. D. and Long P. E. (1981).** Environmental Microbiology. Blackie.
- Greenberg A. E., Conners S. S. and Jenkins D. (1980).** Standard methods for the examination of water and wastewater. American Public Health Association, Washington D. C., 15th ed.
- Grenney W. J., Teuscher M. C. and Dixon L. S. (1978).** Characteristics of the solution algorithms for Qual II river model. J. WCPF. 151-157.
- Hashwa Fuad (1985).** Pollution and biology of surface water in the catchment area of King Talal Reservoir. Dirasat, University of Jordan.
- Hashwa Fuad and Marzolf G. R. (1987).** Seasonal patterns and water quality in King Talal Reservoir, Jordan. Arch. Hydrobiol. 110, 3, 387-397.
- Holm-Hansen O. (1978).** Chlorophyll a determination: improvements in methodology. Oikos 30: 438-447.
- Huang Ching-Sang and Hopson N. E. (1974).** Nitrification rate in biological processes. Journal of Environmental Engineering Division. 100, 409-422.
- Joint Committee of the Water Pollution Control Federation and the American Society of Civil Engineers. (1977).** Wastewater treatment plant design. Lancaster Press Inc.
- Keenan J. D., Steiner R. L. and Fungaroli A. A. (1979).** Substrate inhibition of nitrification. J. Environ. Sci. Health. A14(5), 377-397.
- Knowles G. and Wakeford A. C. (1978).** A mathematical deterministic river-quality model; Part 1: Formulation and description. Water Research Vol. 12, pp. 1149-1153.
- Khoury Norma S. (1986).** Vertical distribution and activities of nitrifying and denitrifying bacteria in King Talal reservoir. An M. Sc. thesis submitted to the Faculty of Science, University of Jordan.
- Kennedy Mark S. and Bell Jhon M. (1986).** The Effects of advanced wastewater

treatment on river water quality. Journal WPCF, Vol. 58, No.12.

Kuchenrither Richard D. et al. (1983). Variable effluent nitrification requirements based on in-stream water quality. J. Water Pollution Control Fed. 55(12), 1489-1496.

Lombardo Pios and Ott Ronald F. (1974). Water quality simulation and application. American Water Resources Association, Vol.10 No.1, pp 1-9.

Mortimer P., Heinz S., Albert B., and Hans G., eds (1981). The Prokaryotes,"A handbook on habitats, isolation, and identification of bacteria. Capter 73, Volume 1. Springer-Verlag. Berlin.

Muela A., Gorostiza I., Iriberi J. and Egea L. (1988). Indicative parameters of denitrification in river sediments. Acta. Hydrochem. Hydrobiol. 16(2), 157-163.

Myers Jack (1946). Culture conditions and development of the photosynthetic mechanism III. Influence of light intensity on cellular characteristics of Chlorella. Gen. Physiol. Vol.29. pp 419-427.

Nakajima Takuo. (1981). Denitrification by Sessile microbes in a polluted river. Verh. Internat. Verein. Limnol. 21(1400-1405) Stuttgart.

ncasi, National Council of the Paper Industry for Air and Stream Improvement INC. (1980). A review of the mathematical water quality model Qual II and guidance for its use. Stream Improvement Technical Bulletin No.338.

Nixon S and Berounsky (1984). Role of nitrification in contributing to low oxygen conditions in an urban water way. Report USGS/6, 867(06). Rhode Island Univ.

Palmer Mervin C. (1980). Algae and water pollution. Castle House Publications.

Parkasam T. B. S. and Loehr R. C. (1972). Microbial nitrification and denitrification in concentrated wastes. Water Research. 6, 859-869.

Peavy S., Rowe, and Tchobanoglous (1987). Environmental Engineering. McGraw

Hill International.

Poch M., Casas C., Lafuente F. J. and Sola C. (1986). Design and calibration of a simplified river - water quality model including heterotrophic bacteria and chemical parameters. *FEMS. Microb. Ecology* 38, 211-218.

Prosser J. I. (1986). Nitrification. Society for General Microbiology.

Prosser J.I. (1990). Advances in microbial ecology, Edited by Marshall K.C., Vol.2. Plenum Press. NewYork

Rozich A. F. and Castens D. J. (1986). Inhibition kinetics of nitrification in continuous-flow reactors. *J. Water Pollution Control Fed.* Vol. 58. pp 220-226.

Saidam M. Y. (1988). Water quality monitoring of esSamra system and Zarka Wadi, and its effect on King Talal reservoir; a case study presented for the regional seminar on the treatment and use of sewage effluent for irrigation. Water Authority of Jordan. Amman.

Salameh Elias and Rimawi Omar (1987). The effects of Khirbet esSamra effluent on the water quality of Wadi Dhuleil and Zerka River, Jordan", Bulletin of the Water Research and Study Center, 10th issue. University of Jordan Press.

Sandoval M., Verhoff, and Cahill (1985). Mathematical modelling of nutrient cycling in rivers.

Sawyer Clair N. and McCarty Perry L. (1978). Chemistry of environmental engineering. McGraw Hill, Kogakusta, Ltd. 3rd Ed.

Schroeder Edward D. (1977). Water and wastewater treatment. McGraw Hill.

Scott J. A. (1981). Benthic oxygen demand. Ph.D. thesis submitted to the University of Exeter, U.K.

Shieh W. K. and La Motta E. J. (1979). Effect of initial substrate concentration on the

rate of nitrification in a batch experiment. *Biotechnology and Bioengineering*, 21, 201-211.

Shima M., Delebeque F. and Adachi N. (1978). A dynamic model of quality of river water with consideration of nitrification process. *Proc. Model Identif. Control Environ. Syst. IFIP Work Conf. Meeting*. 511- 526.

Solorzano L. (1972). Determination of ammonia in natural waters by the phenolhypochlorite method. *Limnology and Oceanography*. 14, pp 799-801.

Starr M. P., Stolp H., Truper H. G., Balows A., and Schlegel H. G. eds. (1981). *The Prokaryotes: A handbook on habitats, isolation, and identification of Bacteria*. Berlin: Springer-Verlag. vol.1.

Sutton P. M., Bridle T. R., Bedford W. K. and Arnold J. (1981). Nitrification and denitrification of an industrial wastewater. *J. Water Pollution Control Fed.* Vol. 53. pp 176-184.

Thomann Robert V. and Mueller Jhon A. (1987). *Principles of surface water quality modelling and control*. Harper and Row Publishers, N. Y.

Tze-Wen Chi and Harold A. (1980). Verifying a water quality model. *US Environ. Prot. Agency off Res. Dev.* 134-41.

U.S. Department of Commerce (1977). Evaluation of nitrification in the water column of the Passaic River. Prepared for office of Water Research and Technology, Washington D. C.

Van-Benschoten J. and Walker W. (1984). Calibration and application of Qual-II to the Lower Winooski River. *Water Resources Bulletin*, American Water Resources Association, Vol. 20, No. 1, 109-117.

WERSC Water and Environment Research and Study Centre (1991). Unpublished

data. University of Jordan, HKJ.

Wild H. E., Sawyer C. N. and McMahon T. C. (1971). Factors affecting nitrification kinetics. Water Pollution Control Fed. Boston. 43(9), pp 516-525.

Wong-Chong G. M. and Loher R. C. (1978). Kinetics of microbial nitrification: Nitrite-Nitrogen oxidation. Water Research. 12, 605-609.

Wong-Chong G. M. and Loher R. C. (1975). The kinetics of microbial nitrification. Water Research. 9, 1099-1106.

Wyer M. and Kay D. (1989). Experimental assessment of rates of nitrate removal by river bed sediments. J. Inst. Water Environ. Manage. 3(3), 273-279.

Yongming Xie. (1988). A Study of nitrification of the Toujiang River. Intern. J. Environ. Sc. Vol. 31, pp. 297-303.

Zison S. W. et al. (1978). Rates, constants, and kinetics formulations in surface water quality modelling. EPA 600/13 78-105. Tetra Tech, Inc. Lafayette, CA.